Organic Semiconductors with High Conductivity. I. Complexes between Polycyclic Aromatic Hydrocarbons and Halogens

By Hideo AKAMATU, Hiroo INOKUCHI and Yoshio MATSUNAGA

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Introduction

Some of the polycyclic aromatic compounds have a pretty good electrical conductivity in the solid state, and from this and other properties they are considered to be organic semiconductors[1]. However, their electrical resistivity at room temperature is of the order of 10^7–10^{12} ohm-cm., even for the most favourable compounds. Hence, it is hoped to learn whether there are any simple organic substances having higher electrical conductivity.

As reported in a preceding paper[2], we have found that some complexes formed between polycyclic aromatic hydrocarbons and halogens have a very good electrical conductivity in the solid state. It is rather surprising to know that such simple organic substances have electrical resistivity as low as 1–10^3 ohm-cm.. Therefore, studies on the electrical properties as well as the structures of these complexes should give us information about the necessary conditions for electrical conduction in organic materials.

Complexes between Polycyclic Aromatic Compounds and Halogens

Brass and Clar[3] have reported that from a benzene solution of perylene, by the addition of bromine, a black coloured precipitate is obtained. Zinke and Pongratz[4] have also found that perylene absorbs bromine vapour directly and changes to a black substance. These authors were in agreement in considering this black substance as a complex or an additive compound formed between perylene and bromine, but there was a little controversy between them over the composition of this substance.

We have found that not only perylene but also most polycyclic aromatic hydrocarbons may form molecular complexes with bromine or iodine, by a method similar to that of Brass and Clar or Zinke.

When we applied Brass and Clar's method, a known quantity of sample was dissolved or suspended in benzene, and an excess amount of bromine or iodine was added to it while boiling the solution. After cooling the solution by itself, the precipitate so obtained was filtered through a glass filter and washed with benzene.

Zinke's method was applied solely to the formation of bromine complex. In this case, a known quantity of sample was taken on a glass filter and put in contact with bromine vapour in a closed glass vessel. The absorption of bromine is completed generally within about ten minutes. After the excess bromine adsorbed is removed by aspiration and dried under reduced pressure, the increased weight of the sample is measured, from which the bromine content of the complex is known.

In the case of bromine complex formation by either method, there occurs a substitution reaction of bromine in the aromatic rings, with simultaneous liberation of hydrogen bromide. This substitution reaction proceeds with a moderate velocity while the complex is forming and continues after the complex is fully formed. This is the reason for confusion about the composition of the complex. Consequently, the apparent bromine content is not fixed but fluctuates in a small range according to the conditions of preparation, even in the case when excess bromine is added to the solution in Brass and Clar's method or when the absorption is completed in Zinke's method. This will be discussed in a later section.

In the preliminary experiments, the following substances were found to form complexes with bromine by Zinke's method. The complex formation is made obvious by the strong colour change and the increment in mass. Benzanthrone (reddish brown), perylene (black), dibromoperylene (black), dibenzoylperylene (brown), distearylperylene (brown), 1, 2-benzperylenequinone (dark brown), anthanthrene (black), mesonaphtho-dianthrone (black), pyranthrene (black), violanthrene

1) H. Akamatu and H. Inokuchi, *J. Chem. Phys.*, **18**, 810 (1950); **20**, 1481 (1952), H. Inokuchi, This Bulletin, **24**, 222 (1951); **25**, 28 (1952); **27**, 22 (1954), D.D. Eley, G. Parfitt, M. Perry and D. Taysum, *Trans. Faraday Soc.*, **49**, 79 (1953).

2) H. Akamatu, H. Inokuchi and Y. Matsunaga, *Nature*, **173**, 168 (1954).

3) K. Brass and E. Clar, *Ber.*, **65**, 1660 (1932); **69**, 1977 (1936).

4) A. Zinke and A. Pongratz, *Ber.*, **69**, 1591 (1936); **70**, 214 (1937).

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(black), violanthrone (dark violet), dibenzpyrene (black), dibenzcoronene (black), and ovalene (black).

The following compounds were found to make complexes with iodine by Brass and Clar's method: perylene (black), violanthrene (black), and dinaphthylene oxide (black).

It was concluded that most of the hydrocarbons can readily form complexes with bromine or iodine and darken their colours nearly to black. Whilst, in the case of quinones, iso-dibenzpyrenequinone could not form a complex with bromine nor iodine, violanthrone formed a complex with bromine but not with iodine. It seems less easy to make them complexes with halogens and even though they form complexes the colour does not change as much as in the case of the hydrocarbons.

The Electrical Conductivity Measurement

The conductance measurement was made by the potential drop method in the following conditions. The sample powder was packed in an ebonite cylinder and attaching to each end a silver coated metallic cap, compressed under about 200 kg. per cm^2 pressure.

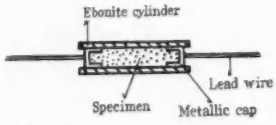


Fig. 1. Specimen cell for the conductance measurement.

It was found that most of the black complexes cited above show good conductance. The values of resistivity lie between about 5 ohm-cm of dibromoperylene-bromine complex and about 900 ohm-cm of dinaphthylene oxide-iodine complex. However, the resistivity is not stable and increases rapidly at first and then gradually over a period of days. The values cited above are that of the freshly prepared specimens, as the resistivity increases to kilo ohm-cm after several weeks even in the case of dibromoperylene-bromine complex. The features are shown in Fig. 2. The reason for this instability of resistivity will be considered in detail in the following section.

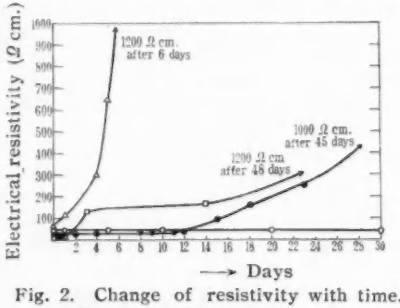


Fig. 2. Change of resistivity with time.
- ● Perylene-bromine
- ○ Violanthrene-iodine.
- □ Dibromoperylene-bromine
- △ Violanthrene-bromine.

There is one further problem to be considered concerning the observed conductance, that is the question whether it is an intrinsically electronic conductance or not.

It was found, during the measurement of resistivity, that after application of the potential through the specimen cell, the cell itself developes a small electromotive force of a few millivolts in a direction opposite to the applied potential. Therefore, a part of the conductance at least must be attributed to ionic conductance. The resistivity due to the ionic conductance (R_i) and that due to the electronic conductance (R_e) can be separately estimated by the following way. Assuming the total resistivity (R) which is measured in the usual way, to be made up of R_e and R_i in parallel, then $1/R=1/R_e+1/R_i$, where R_i can be estimated from the current which results from the electromotive force of the specimen cell itself, without any applied potential from outside, measured by reference to a standard resistor. In most cases, the conductance due to ionic ($1/R_i$) is 10–20 per cent of the total conductance for fresh specimens and thereafter decreases to 5 per cent or less. The remainder is assumed to be electronic conductance ($1/R_e$). If we take the value of R_e, they were found to be more stable than R itself. In Fig. 2, the R_e is plotted as a function of time (days).

Furthermore, it was soon found that if moisture is carefully excluded and the specimen is made from a thoroughly dried sample, the ionic conductance part decreases to an almost undetectable value. Therefore the larger part of the observed conduction may be considered as due to the electronic conductance. All values cited in the present paper, however, are those R_e calibrated in the above way.

Further evidence against ionic conduction can be obtained by the following consideration. A specimen of violanthrene-iodine complex, as an example, contained 150 mg. of iodine as its component. If the observed current is wholly due to electrolytic conduction, it must drop within sixteen minutes after the current of 120 mA has passed

through the cell. It did not do so, however, and the stable current was observed as long as five hours or more, excepting a small drop in resistance which is due to the thermal effect of the current. This latter drop in resistance recovered to the initial value after the current was ceased.

The Conductivity of Perylene-Bromine Complex

The resistivity of perylene-bromine complex is several ohm-cm at the freshly prepared state, but it changes over a period of days and increases to 10^3 ohm-cm. or more after several weeks. Therefore, it must be ascertained whether the nature of conduction itself is so unstable or the complex itself is unstable and changes its structure. Concerning the latter possibility, in the case of the bromine complex the liberation of hydrogen bromide is observed as mentioned above. This is due to the substitution reaction of bromine. Therefore, the specimen is in a dynamic state in which a part of bromine combined as the molecular compound at the beginning takes place substitution reaction to make bromoperylene and at the same time the equivalent bromine is liberated as hydrogen bromide. Moreover, decomposition is caused in the specimen cell at the place of contact of the metallic electrodes.

Hence, the electrical resistivity as a function of the composition was investigated in the following way. A set of samples of perylene-bromine complex was made by Zinke's method. Their composition was one perylene molecule to nearly four bromine atoms in the fresh state. Specimen cells for the conductivity measurement were made using parts of these samples, and the resistivity was measured in as fresh a state as possible. The resistivity and the bromine content of these specimens are shown by the points of 1, 2, and 3 in Fig. 3. The remaining parts of the samples were preserved in a desiccator over potassium hydroxide. At an appropriate period of days, the decrease in mass of the preserved samples was measured. From this the bromine content was determined, and at the same time the resistivity was measured, using a part of the sample. The resistivities thus obtained as the function of the bromine content are shown in Fig. 3 by the points of 4, 5, etc.

When the sample in which the bromine content had decreased was put into bromine vapour, it absorbed bromine again and its conductivity recovered to a certain degree. This is shown in Fig. 3 by the points of 4′, 5′, etc., (concerning these points, the bromine content on the abscissa has no meaning).

From this investigation, it is understood that the instability of the conductivity of the complex is due to the change of the bromine content of the complex itself.

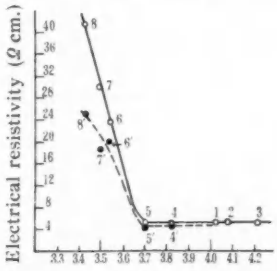


Fig. 3. Electrical resistivity of perylene-bromine complex as the function of total bromine content.

Perylene-bromine complex decomposes spontaneously as mentioned above. The change of the total apparent bromine content through a period of days, for an example, is shown in Fig. 4. If it is assumed that the decomposition is solely due to the substitution reaction to make dibromoperylene, the reaction is

$$(C_{20}H_{12}\text{-}4Br) \longrightarrow C_{20}H_{10}Br_2+2HBr.$$

Hence, the complex of which the apparent composition is one perylene molecule to n bromine atoms is in fact made of dibromoperylene-bromine complex and perylene-bromine complex. This is expressed by

$$(C_{20}H_{12}\text{-}nBr) \simeq \alpha C_{20}H_{10}Br_2 + (1-\alpha)C_{20}H_{12} + (n-2\alpha)Br.$$

The amount of the additively combined bromine can be estimated, and distinguished from substituted bromine, by titration with sodium thiosulphate solution. In the case shown in Fig. 4, n was 4.03 in the fresh complex and it changed to 3.30 at a final

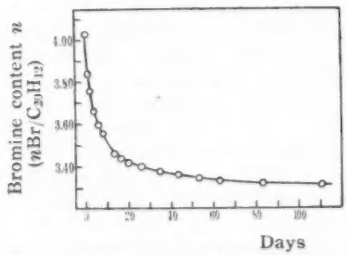


Fig. 4. Change of total bromine content following the decomposition of perylene-bromine complex.

state after the decomposition had proceeded. In this final complex, the content of the free bromine was found to be 0.97 atoms per one perylene molecule, consequently 2.33 atoms were substituted bromine. During this decomposition process, 0.73 bromine atoms per one perylene molecule were lost and the equivalent amount had been substituted, therefore, the content of bromine as dibromoperylene contained in the initial fresh complex was 1.60 (=2.33−0.73) atoms per one perylene molecule. This means $\alpha=0.8$ in the above scheme.

The complex of which the apparent composition is one perylene molecule to 4 bromine atoms was in fact a mixture of 80 per cent of dibromoperylene dibromide and 20 per cent of perylene tetrabromide, even in the initial fresh state. From this it is understood that the substitution reaction of bromine is relatively rapid at least at the beginning, and a large part of the perylene changes to dibromoperylene during complex formation. The resistivity of the "perylene-bromine (1 : 4) complex" agrees well with that of dibromoperylene-bromine (1 : 2) complex, both in the fresh state, and is about 5 ohm-cm.

Dibromoperylene dibromide, further changes to tetrabromoperylene with simultaneous liberation of hydrogen bromide,

$$2(C_{20}H_{10}Br_2-2Br)\rightarrow C_{20}H_8Br_4 + C_{20}H_{10}Br_2+2HBr.$$

With the progress of this reaction, the content of the additively combined bromine is progressively lost. Hence, passing the point 5 in Fig. 3, all perylene molecules have changed to dibromoperylene and thereafter only the above reaction takes place, at the same time the conductivity of the complex begins to decrease rapidly. In this stage, the reabsorption of bromine leads to a recovery of the conductivity in a certain limited degree, but not completely. This is due to the formation of the additive compound between dibromoperylene and bromine, but it is supposed that tetrabromoperylene can scarcely form a complex.

It is concluded that the instability or decrease in the conductivity of the complex is due to the loss of bromine which combines to form the additive compound. In other words, the origin of the conductivity is attributed to the interaction between a molecule of perylene or its bromine derivative and additively combined bromine molecules.

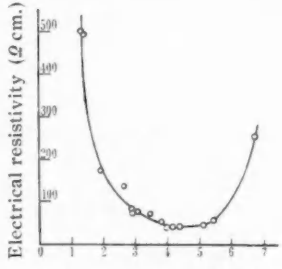
Violanthrene-Iodine Complex

If there is any system in which the substitution reaction of halogen does not take place, such a complex will be stable of itself as well as of electrical property. It was found that the violanthrene-iodine complex is such a case.

This complex was made by Brass and Clar's method. About 600 mg. of violanthrene were suspended in 50 cc. of benzene, and boiled with 5 g. of iodine. The suspension was precipitated, forming the complex. Since the solubility of violanthrene in benzene is negligibly small, the increased weight of the precipitate was assumed to be due to the iodine content of the complex formed, from which the composition was determined as one violanthrene molecule to 4 iodine atoms. However, the composition can be varied by controlling the ratio of violanthrene to iodine, adding more or less.

The mass of this complex did not change when it was kept in a desiccator, therefore it was concluded that no decomposition takes place. Furthermore, it is quite stable up to 60°C. When it is heated beyond this temperature in a sealed glass tube, it is observed that iodine vapour is liberated. However, the recombination of iodine takes place spontaneously when it is cooled down.

The conductivity of violanthrene-iodine complex is quite stable and does not show any change over a period of weeks. The resistivity as the function of the composition is shown in Fig. 5. In this figure, it is seen that the maximum conductivity is attained at the composition of $n=4$, beyond this composition the conductivity again begins to decrease. It is assumed that in the range of the composition up to $n=4$, iodine content is insufficient to make up the additive compound with all molecules of violanthrene, whilst beyond $n=4$ excess iodine molecules are present, in some other state than the above additive compound, they fail to contribute to the conduction, giving rise to an insulating effect. Hence, 4 iodine atoms per



Iodine content n ($nI/C_{34}H_{18}$)

Fig. 5. Electrical resistivity of violanthrene-iodine complex as the function of the composition.

one violanthrene molecule is the saturation value of the composition of this additive compound and its resistivity is about 40 ohm-cm. at room temperature.

The Temperature Coefficient of the Resistivity

The temperature dependence of the resistivity was measured, for some complexes, in the range from room temperature down to the temperature of liquid air. The resistivity increases with decreasing temperature and a good linear relationship was observed between the logarithm of the resistivity and the reciprocal of temperature, as expressed in $\rho=\rho_0 \exp(\Delta\varepsilon/2kT)$ where ρ is the resistivity and $\Delta\varepsilon$ is the energy gap for conductivity. An example of the results is shown in Fig. 6, for violanthrene-iodine complex. The behaviour is as found with typical semiconductors. In Table I the values of $\Delta\varepsilon$ of the complexes are shown referring to $\Delta\varepsilon^*$ of the corresponding hydrocarbons. The decrement in the energy gap for conductivity is remarkable when the mole cular complex is formed.

Discussion

Among simple organic substances, excepting graphite or carbons, no substance has ever been known with so high an electrical conductivity as in the present case. Violanthrene itself is assumed to be an intrinsic semiconductor, but its resistivity is still 2×10^{14} ohm-cm., and the resistivity of perylene is presumably more than 10^{22} ohm-cm. It is concluded that the high conductivity of the complexes between polycyclic aromatic hydrocarbons and halogens is due to an appropriate electronic state following the formation of the additive compound. Hence, in such a state, it must be assumed that there are strongly labile electrons and they can transfer from molecule to molecule under the influence of an electric field.

TABLE I
SEMICONDUCTIVITY DATA OF COMPLEXES

Complex	Resistivity at room temp. (ohm-cm.)	Temp. range (°C.)	$\Delta\varepsilon$ (eV.)	$\Delta\varepsilon^*$ (eV.)
Perylene-bromine (1 : 4.4)*	7.8	−20∼−170	0.13	—
Pyranthrene-bromine (1 : 3.3)	220	〃	0.20	1.07
Violanthrene-bromine (1 : 4.5)	66	〃	0.20	0.85
Violanthrene-iodine (1 : 4.0)	45	〃	0.15	〃
Violanthrene-iodine (1 : 4.0)	45	10∼60	0.14	〃

* The composition is an apparent one, expressed in one hydrocarbon molecule to halogen atoms.

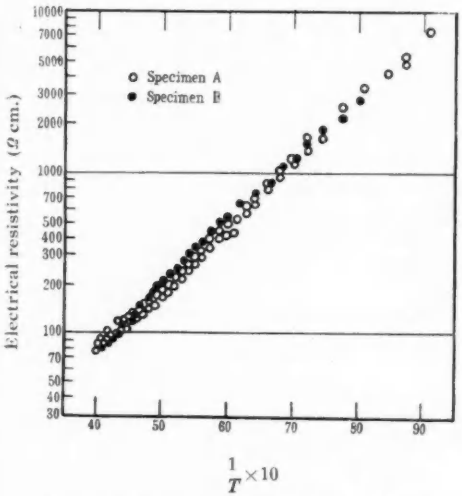


Fig. 6. Temperature dependency of resistivity of violanthrene-iodine complex.

It is known that in benzene solution of iodine, a complex formation takes place between a benzene molecule and an iodine molecule. Mulliken[5] pointed out the possibility of the intermolecular charge transfer force between them, from the presence of the corresponding spectrum, that is to say, an electron transfer takes place from a benzene molecule toward an iodine molecule accompanied by an overlapping of the molecular orbitals. The formation of the present complexes can be assumed to be due to the similar force as in the case of benzene-iodine complex. However, there is a noteworthy difference between these two cases.

In a benzene solution of iodine, a stoichiometric one to one molecular complex is formed in a state isolated from each other. On the other hand, in the present case the complexes are formed in the crystalline state, in which the molecular orbital for any one

5) R.S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

molecule might overlap, if possible, with those of more than one of its neighbours. Moreover, the stoichiometric relationship is not necessarily fulfilled. In the case of violanthrene-iodine complex, the relative composition is 1:4 in the saturated state. Nevertheless, in fact, in the range where the iodine content is far less than this ratio, the complex still has a pretty good conductance. Hence, in this range of composition, it would not be a mechanical mixture of violanthrene tetraiodide and violanthrene, but it would be a non-stoichiometric molecular compound as a whole, in which iodine molecules are distributed among violanthrene molecules or vice versa. In such a state, there is not a one to one correspondence between violanthrene molecules and iodine molecules.

In the present complexes, the bond character between a hydrocarbon molecule and a halogen molecule is presumably far from an ionic one, and even from a dative covalent bond, and it might be shifted to the more metallic-like bond with delocalized electrons. Such a bond character might be attributed to an appropriate balance between the low ionization potential of a hydrocarbon molecule, which decreases with an increasing number of aromatic rings, and the high electron affinity of the halogen molecule.

Results from magnetic susceptibility measurements show that the presumable diamagnetism decreases and the paramagnetism increases, from which the presence of non-paired electrons is predicted. The details of the magnetic measurements has been presented by one of us[6].

When examined by X-rays, violanthrene-iodine complex gives merely a very diffused amorphous pattern. This agrees with the discussion mentioned above. On the other hand, in the case of perylene-bromine complex, the X-ray diffraction pattern is made of sharp lines, of which the features are varied according to the relative composition of the complex. Hence, the non-stoichiometric or amorphous state is not necessary for conductance.

Recently, Holmes-Walker and Ubbelohde[7] have reported that complexes formed between anthracene and alkali metals show semiconductor behaviour with electrical conductivity ranging 10^{-8}–10^{-12} (ohm-cm.)$^{-1}$. It was suggested that the complexes are formed by a non-stoichiometric electron transfer between alkali metal atoms and hydrocarbon molecules.

Besides these molecular complexes, even the polycyclic aromatic compounds themselves show semiconductor behaviour, and their resistivity decreases with an increase in the number of aromatic rings. In this case, it can be assumed, analogous to the complexes, that each molecule behaves as an electron-donor or electron-acceptor, one by one, and a sort of inner complex is formed between the same kind of molecules in the crystalline state.

All of these cases suggest strongly that there takes place an intermolecular overlapping of the molecular orbitals stretching throughout the crystal, whilst the molecular crystals are commonly considered as being held together merely by the force of van der Waals type between the molecules.

Summary

It was found that most polycyclic aromatic hydrocarbons form molecular complexes with bromine or iodine. Those complexes which are black behave as typical semiconductors with energy gaps for conductivity of 0.1–0.2 eV., as well as with low electrical resistivity ranging from 10^{0} to 10^{7} ohm-cm. The complexes are unstable and a substitution reaction of halogen takes place; when this is not the case, e. g. the violanthrene-iodine complex, and the complex itself is quite stable, so also is the electrical property. It is concluded that the origin of the high conductivity is due to the interaction between hydrocarbon molecules and halogen molecules, and this is presumably due to the overlapping of molecular orbitals stretching throughout the crystal.

The cost of this research has been defrayed from the Grant in Aid for Fundamental Scientific Research from the Ministry of Education, to which the authors' thanks are due.

Department of Chemistry, Faculty of Science, The University of Tokyo, Tokyo

6) Y. Matsunaga, This Bulletin, **28**, 475 (1955).
7) W.A. Holmes-Walker and A.R. Ubbelohde, *J. Chem. Soc.*, **1954**, 720.

Paper Chromatography of Radioactive Substances. (Radiochemical Studies on "Bikini Ashes" (March 1, 1954), Part III). (Studies of the Analytical Chemistry on Filter Paper XVI)

By Shoichi NAKANO

(Received August 4, 1955)

Since Consden, Gordon and Martin[1] found in 1944 that filter paper sheets can be used as support of a stationary phase in partition chromatography, radioactive tracer techniques are applied to the identification of the substances developed on paper without the aid of reagents. For example, Wieland et al.[2] determined amino-acids by chromatographing their Cu salts containing radioactive Cu.

The methods for the separation of radioactive substances by means of ion exchange resins developed very rapidly by the studies carried out in connection with the work on atomic energy in the U. S. A.[3-13]. Tompkins, Khym and Cohn[14] found that a mixture of fission products which passed through a column of Amberlite IR-I (HR-form) to separate anions could be further separated into three groups by washing the column with oxalic acid to remove Zr and Hf, then with citrate at pH 3 to remove rare earths, and then with citrate at pH 5 to remove alkaline earths.

On the other hand, the separation of radioactive substances by paper chromatography has also been studied by several workers, but not so fully as ion exchange resins. For example, radioactive ^{42}K and ^{24}Na were separated by Frierson and Jones[15]. Bouissieres and Lederer[15] separated Ra and Ba using ethanol- water (80 : 20) as solvent, ^{22}Na and Mg with ethanol-20% water. By paper electromigration, Sato, Norris and Strain[17] obtained a good separation of many radioactive elements with 0.1 M lactic acid. In Japan, the separation of the radioactive substances adhering on the surface of tunny was also studied with the aid of paper chromatography by Kiba et al[18].

As above mentioned, the separation of radioactive substances by paper chromatography has not been investigated in detail, therefore many problems remain to be solved in a fundamental field. The important variables which have influence on the degree of separation, R_f values, purity and spot shape are: (I) carrier and its quantity; (2) other inactive substances (such as scavenger, analogous element, impurities in paper and solvent); (3) filter paper; (4) solvent; (5) self-absorption of radiation in paper (thickness of paper)[19]; (6) quantity spotted on original point; (7) temperature.

The author studied paper chromatography of radioactive substances in connection with ion-exchange resins so as to examine these effects in detail.

Experimental and Results

Separation by Ion-exchange Resins into four Groups.—According to Tompkins, Khym and Cohn[14], a mixture of fission products are separated into about four groups, and the nuclides in each group are further separated by ion exchange resins. The author tried the separation of nuclides in each group, which had been previously separated by ion exchange resins as shown in Fig. 1, with the aid of paper chromatography. The author treated the nuclides which are described in each group in Fig. 1. The obtained result is as follows.

Filter Paper.—Sheets of the Toyo filter paper

1) R. Consden, A. H. Gordon and A. J. P. Martin, *Biochem. J.*, 38, 224 (1944).
2) T. Wieland, K. Schmeiser, E. Fischer and H. Maier-Laibnitz, *Naturwissenschaften*, 36, 280 (1949).
3) B.H. Ketelle and G.E. Boyd, *J. Am. Chem. Soc.*, 69, 2800 (1947).
4) F. H. Spedding, *Discuss. Faraday Soc.*, 7, 214 (1949).
5) L.B. Werner and I. Perlman, *USAECD*, 1898.
6) S.G. Thompson, R. A. James and L. O. Morgar, *USAECD*, 1907.
7) K. Street Jr. and G.T. Seaborg, *J. Am. Chem. Soc.*, 72, 2790 (1950).
8) S.G. Thompson, B.B. Cunningham and G.T. Seaborg, ibid., 72, 2798 (1950).
9) K. Street Jr., S.G. Thompson and G.T. Seaborg, ibid., 72, 4832 (1950).
10) L.B. Magnusson, S.G. Thompson and G.T. Seaborg, *Phys. Rev.*, 78, 363 (1950).
11) R. Bouchez and G. Kayas, *Compt. rend.*, 228, 1222 (1949).
12) G. Kayas, *J. Chim. Phys.*, 47, 408 (1950).
13) E.R. Tompkins, ibid., 70, 3520 (1948).
14) E.R. Tompkins, J.X. Khym and W.E. Cohn, *J. Am. Chem. Soc.*, 69, 2769 (1947).
15) W.J. Frierson and J.W. Jones, *Anal. Chem.*, 23, 1447 (1951).
16) G. Bouissieres and M. Lederer, E. Lederer, M. Lederer and A.T. James, "Chromatography", Elsevier Publishing Co., Amsterdam, (1954), p. 331.
17) T.R. Sato, W.P. Norris and H.H. Strain, *Anal. Chem.*, 26, 267 (1954).
18) T. Kiba, S. Ohashi, M. Sibata and T. Mizube, *Japan Analyst*, 3, 361 (1954).
19) F. P. W. Winteringham, A. Harrison and R.G. Bridges, *Analyst*, 77, 19 (1952).

No. 5A or No. 5B (40×32 cm., with up to 8 samples on one sheet) are commonly used so as to prevent the influence of paper. When the development is completed (25 cm.), the sheet is hung for drying andc ut into strips (4×32 cm.) for measurement.

mm. in width and trailing the paper strip 10 mm. to every five minutes. Furthermore, the determination of each nuclide is done by the use of Nuclear Type 183, G. M. Counter having a mica window with a thickness of 1.4 mg./cm².

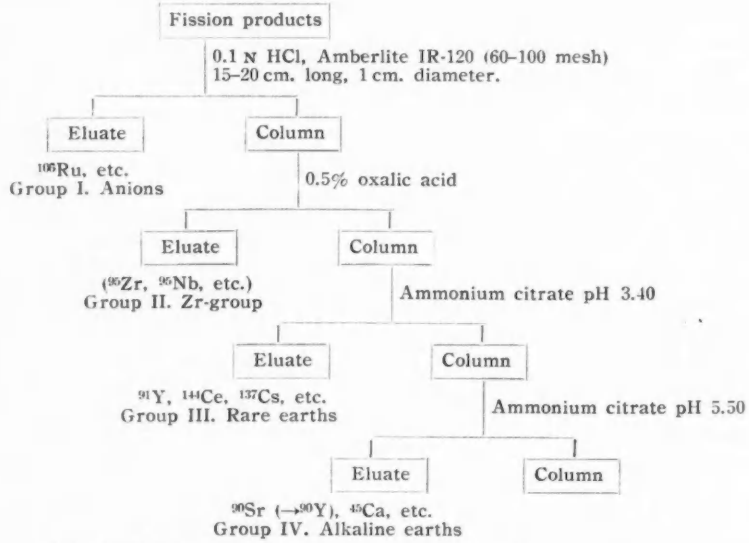


Fig. 1. Separation by ion exchange resins into four groups.

Test Solution.—The test solution separated from ion exchange resins or by distillation are concentrated to 3–10 cc. on the water bath, therefore, those solutions contain ammonium citrate, etc. (pH about 2–6).

Measurement of Radioactivity.—The distribution of radioactive substances on filter paper is measured by the Lauritzen electroscope with the author's continuous scanning device as shown in Fig. 2. It consists of lead plate (3 g./cm²) with paper holder and a slit which can be regulated by a screw. It is inserted into the gutter of the ionization chamber, and a filter paper strip is moved between the slit and the holder.

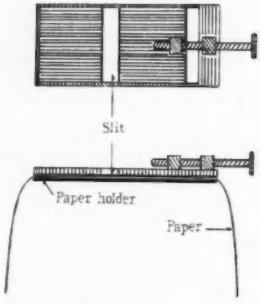
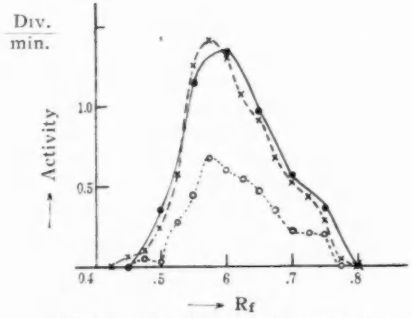


Fig. 2. Scanning slit of lead plate.

As shown in Fig. 3, it was observed that the best result is obtained by keeping the slit to 10



Methanol 9, c. NHO_3 1, Toyo filter paper No. 5B 15°–16°C, 4 hr./25 cm.

Fig. 3. Measurement of radioactivity using Lauritzenelectroscope.

- •—•—• Slit: 10 mm. in width, trailing; 10 mm./5 min.
- ○···○···○ Slit: 10 mm. in width, trailing; 5 mm./5min.
- ×···×···× Slit: 10 mm. in width, trailing: 5 mm./5 min.

(1) Separation of Group I (Anions).—At first, the author tried the separation of anions by using a sample solution separated with the aid of ion exchange resins from "Bikini Ashes" by the above mentioned method on May 24, 1954 (Fig. 4). Iso-amylalcohol-HCl (74:26) was used

as solvent. But the radioactivity was so low that nuclides could not be determined thoroughly. ^{35}S was reported on June 25, 1954 by the Tokyo University later.

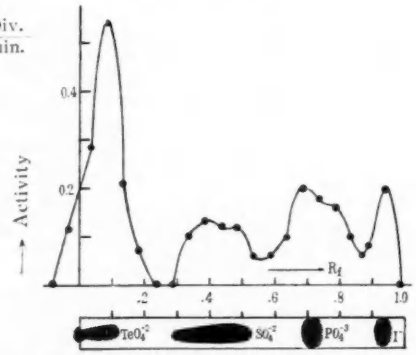


Fig. 4. Radio-chromatogram of anions (Group I).

iso-Amylalcohol	74
conc. HCl	26

Toyo filter paper No. 5A; 22°C.; 22 hr./25 cm. (SO_4^{-2} and PO_4^{-3} could be detected by chemical reactions.)

Fig. 5 is the radio-chromatogram of carrier-free ^{106}Ru separated from "Bikini Ashes" and ^{235}U-fission products by ion exchange resins. It is interesting that ^{106}Ru appears at two separated spots. As shown in Fig. 6, however, ^{106}Ru is detected as a spot extending over the whole paper with methanol-HNO_3 (9:1). This figure contains the radio-chromatograms of carrier-free ^{106}Ru derived from ion exchange resins and the distillation method.

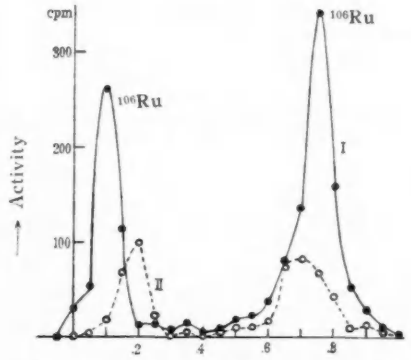


Fig. 5. Radio-chromatograms of ^{106}Ru (Group I).

iso-Amylalcohol	74
conc. HCl	26

From "Bikini Ashes". Quantity spotted on O.P.:
I: Large amounts.
II: Small amounts.
The same result was obtained in respect of a sample from ^{235}U-fission products.

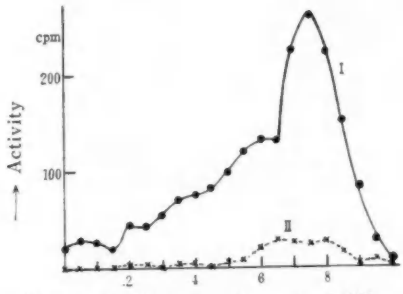


Fig. 6. Radio-chromatograms of ^{106}Ru.

Methanol	9
conc. HNO_3	1

Toyo filter paper No. 5B.
Sample solution: I: From ion exchange resins: II: From distillation.

(2) Separation of Group II(Zr-group).—The author has not obtained results to report here about this group yet, because the test solution was used for an other experiment by another student.

(3) Separation of Group III(Rate Earths).—A sample solution separated with the aid of ion exchanger from ^{235}U-fission products by the above mentioned method was developed with methanol-HNO_3(9:1). It is observed clearly in Fig. 7 that ^{137}Cs (alkali metal) is contained within this portion of eluates from the ion exchanger, and that ^{144}Ce and ^{137}Cs are separated completely. But also that ^{137}Cs was not found in the "Bikini Ashes" by this method.

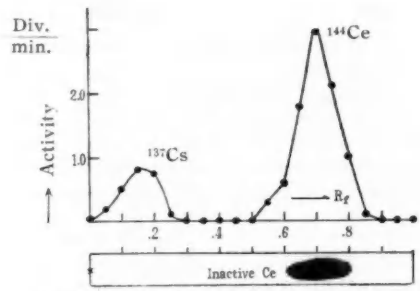


Fig. 7. Radio-chromatogram of rare earths (Group III).

Methanol	9
conc. HNO_3	1

Toyo filter paper No. 5B; 15°–16°C.; 4 hr./25 cm.
From ^{235}U-fission products.

A radio-chromatogram of ^{91}Y obtained from "Bikini Ashes" using ion exchange resins is shown in Fig. 8.

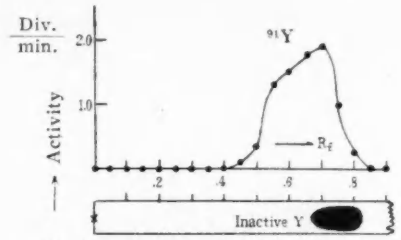


Fig. 8. Radio-chromatogram of rare earths (Group III).

{Methanol 9
{conc. NHO_3 1

Toyo filter paper No. 5B; 15°–16°C; 4 hr. /25 cm. From "Bikini Ashes".

In both chromatograms developed with methanol-HNO_3 (9:1), R_f values of carrier-free ^{144}Ce and ^{91}Y agree with R_f values of inactive Ce and Y nitrates (spot on paper strip in figure, R_f=0.70 and 0.75 respectively). When 1% oxine in glacial acetic acid is used as solvent, however, R_f values of carrier-free radioactive ^{144}Ce and ^{91}Y are not in agreement with R_f values of inactive Ce and Y respectively. In Figs. 9 and 10, ^{144}Ce containing ^{137}Cs and ^{91}Y are developed with 1% oxine in glacial acetic acid. In Fig. 9, inactive Ce separates to two spots (R_f=0.00 and 0.86), but carrier-free radioactive ^{144}Ce travels to R_f=0.85 only. The behavior of ^{144}Ce containing inactive Ce as carrier has also a different appearance as shown later. The peak of R_f=0.5–0.65 may be due to ^{137}Cs. In Fig. 10, the peak of ^{91}Y is found at R_f=0.30, but inactive Y has an R_f=0.48.

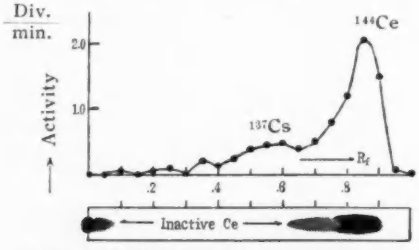


Fig. 9. Radio-chromatogram of rare earths (Group III).

1% oxine in gl. acetic acid. Toyo filter paper No. 5A; 15°–16°C; 5 hr./25 cm. From ^{235}U-fission products.

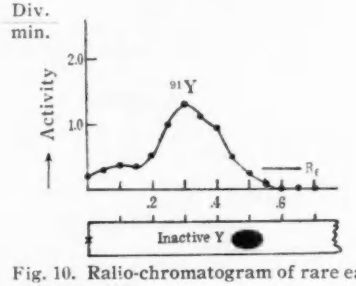


Fig. 10. Ralio-chromatogram of rare earths (Group III).

1% oxine in gl. acetic acid. Toyo filter paper No. 5A; 15°–16°C; 5 hr./25 cm. From "Bikini Ashes".

(4) Separation of Group IV (Alkaline Earths).—The typical results of separation of alkaline earths using methanol-HNO_3 (9:1) or 1% oxine in glacial acetic acid as solvent are shown in Figs. 11, 12, 13 and 14. A sample solution of carrier-free ^{90}Sr (containing ^{90}Y as its daughter) was separated by means of ion exchange resins from ^{235}U-fission products by the above mentioned method. A solution of ^{45}Ca was obtained from the liver of a tunny and separated using ion exchanger. It may contain inactive Ca. But the radioactivity was so low that ^{45}Ca could not be determined thoroughly (whether 0.7–0.8 or 0.0–0.4). In case of methanol-HNO_3 (9:1), R_f values of radioactive carrier-free ^{90}Sr, ^{90}Y and pure ^{90}Y separated from ^{90}Sr nearly agree with R_f values of inactive Sr and Y. In case of 1% oxine in glacial acetic acid, however, R_f values of radio-

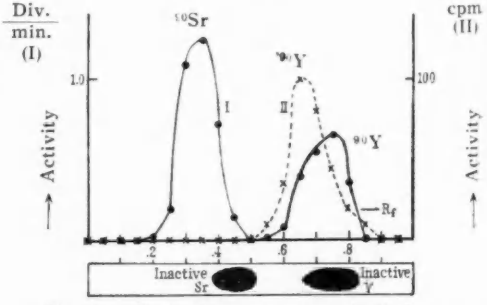


Fig. 11. Radio-chromatogram of alkaline earths (Group IV).

{Methanol 9
{conc. HNO_3 1

Toyo filter paper No. 5B; 15°–16°C; 4 hr. /25 cm. From ^{235}U-fission products.
I; ^{90}Sr containing ^{90}Y. II; Pure ^{90}Y.

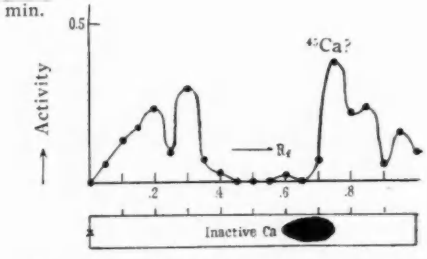


Fig. 12. Radio-chromatogram of alkaline earths (Group IV).

Toyo filter paper No. 5B; 4 hr./25 cm. From liver of tunny.

{Methanol 9
{conc. HNO_3 1

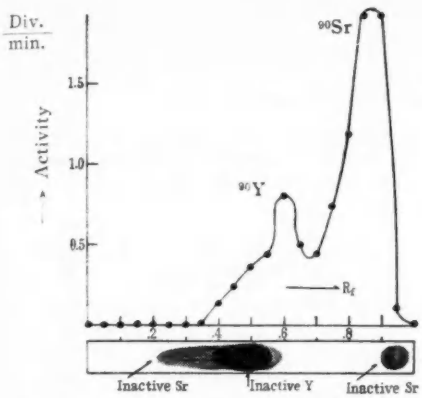


Fig. 13. Radio-chromatogram of alkaline earths (Group IV).
1% oxine in gl. acetic acid. Toyo filter paper No. 5A; 15°–16°C; 5 hr./25 cm.
From ^{235}U-fission products.

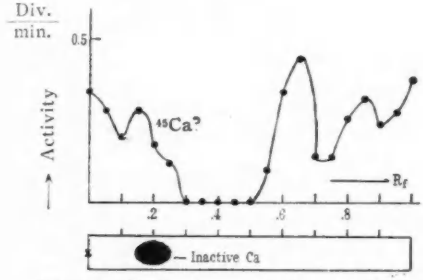


Fig. 14. Radio-chromatogram of alkaline earths (Group IV).
1% oxine in gl. acetic acid. Toyo filter paper No. 5A; 15°–16°C; 5 hr./25 cm.
From liver of tunny.

active and inactive elements are different from those shown in Fig. 13. That is, ^{90}Sr travels to R_f=0.87 which corresponds to one of the spots of inactive Sr (R_f=0.40 and 0.95), and R_f values of radioactive ^{90}Y and inactive Y are 0.60 and 0.45 respectively. The position of ^{45}Ca could not be determined as low counts in both of the solvents. In addition, as shown in Figs. 10 and 13 with 1% oxine in glacial acetic acid, it is interesting that R_f values of radioactive ^{91}Y, ^{90}Y and inactive Y are 0.30, 0.60 and 0.45 respectively.

(5) Influence of Carrier or other Elements.— As above shown, in 1% oxine in glacial acetic acid, the behavior of radioactive elements differs from that of the inactive elements. Therefore, it is very clear that the existence of carrier or other elements have some influence upon R_f value of a radioactive element. The qualitative results obtained are shown in Fig. 15. In this experiment, 1% oxine in glacial acetic acid is used as solvent. The strips ,a, b and c in Fig. 15 represent the movements of inactive Ce, ^{144}Ce (containing

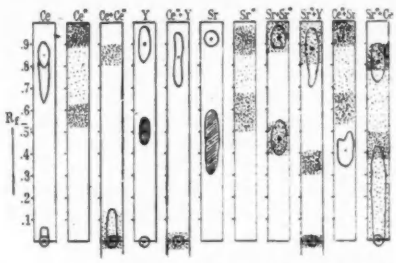


Fig. 15. Influence of carrier or other elements.
1% oxine in gl. acetic acid. Toyo filter paper No. 5A; 15°–16°C. 5hr./25 cm.
Ce* contains Cs*. Sr* contains ^{90}Y.

: Represents inactive element (Ce, Y and Sr).
: Represents position of a large part of ion.
* : Represents radioactive elements.
: Represents radioactivity

^{137}Cs), and ^{144}Ce with inactive Ce as carrier respectively. These strips show the influence of the carrier on ^{144}Ce containing ^{137}Cs (radioactivity of an R_f of 0.00). From the strips, b, d and e, it is clear that an addition of inactive Y to ^{144}Ce alters the R_f of ^{144}Ce remarkably. The results with respect to Sr and ^{90}Sr (containing ^{90}Y) are shown in the strips, f, g and h. The influence of inactive Y and Ce upon radioactive ^{90}Sr are remarkable as shown in the strips, i and k. This phenomenon may be due to ^{90}Y in ^{90}Sr. There is no influence of inactive Sr on ^{144}Ce (containing ^{137}Cs), and the former is not detected at R_f=0.92 (the strip, j). But a limit of detection of inactive Sr, as above inactive Ce and Y, is a question.

Discussion

The present author studied the paper chromatography of radioactive substances in connection with ion exchange resins, and obtained the results that nuclides can rapidly be determined by applying the paper chromatography to the separation of radioactive elements of the four groups eluated from ion exchange resins. In particular, the author knew that the factors influencing on R_f value and degree of separation of radioactive substances are (1) carrier or analogous element; (2) quantity spotted on original point of filter paper. These effects are shown in Figs. 15 and 5. Furtheremore, the R_f values of inactive and active elements are generally ^{144}Ce≤Ce (inactive) (Fig. 7); ^{90}Sr<Sr (inactive), ^{90}Y<Y (inactive) (Fig. 11) in methanol-HNO_3, and are ^{144}Ce≤Ce (Fig. 9); ^{91}Y<Y (Fig. 10); ^{90}Sr<Sr, ^{90}Y>Y (may be due to ^{90}Sr, Fig. 13) in 1% oxine in glacial acetic acid. That is, as shown in the reports with respect to

the influence of cations on the R_f values of anions (Cl^-, NO_3^- and SO_4^{2-})[20], the R_f values of the element of a large mass are smaller than those of the element of a small mass. But it can not be concluded in these experiments that the difference of an R_f of inactive and active element is due to a mass number. Because a difference of quantity spotted on the original point of paper between inactive and active solutions, a different complex formation in very dilute solution and the existence of some other substance in an active sample solution (ammonium citrate) in place of nitrate of inactive sample solution. It is the author's wish to study these questions quantitatively.

The author wishes to express his heartfelt thanks to Prof. Takanobu Siokawa, Sizuoka University, for his kind advice and encouragement.

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20) S. Nakano, *J. Chem. Soc. Japan*, **75**, 150 (1954).

Über den Mechanismus von Goldsensibilisierung der Photographischen Emulsion. II. Die Einflüsse von Gold bzw. Goldverbindungen auf die Lichtelektrische Leitfähigkeit des Silberbromides. I

Von Keiichi YAMADA, Shumpei OKA und Takashi MUKAIBO

(Eingegangen am 27. September, 1955)

Einleitung

Der erste Teil dieser Untersuchungen[1] zeigt, daß der Ersatz durch Gold von den in od. auf dem Silberbromid sich befindenden Silberkeimen auch von dem Gesichtspunkt der Elektronenbeugung höchst wahrscheinlich ist.

Der zweite Teil hat also die Rolle dieser Goldkeimen beim Lichtempfindungsprozeß klar in stellen.

Es ist vorher behauptet worden, daß diese Goldkeime als Elektronen- od. Elektronendefektstellen-Fallen stärker als Silberkeime wirken. Wenn diese Vermutung zu recht besteht, muss die Veränderung an der Bewegung von Elektronen bzw. Ionen auf die elektrische Leitfähigkeit des Kristalls irgendeinen Einfluß ausüben. Der Zweck dieser Untersuchung ist folglich, durch die Messung von lichtelektrischer Leitfähigkeit vor und nach dem Zusatz von Goldkeimen, einige Kenntnisse davon zu erlangen.

Experimentelles

(1) Herstellung der Präparate. — Das auf 500–520°C geschmolzene Silberbromid wurde in die Spalte zwischen zwei Glasplättchen (25 mm. × 75 mm.) eingegoßen. Nach langsamer Abkühlung wurde das entstandene Polykristall im Wasser von den Glasplättchen abgezogen. Aus dem so hergestellten Polykristall wurden 6–7 Stücke von Proben genommen.

(2) Apparatur und Messmethodik. — Die Messung von dem lichtelektrischen Strom wurde mit einen Röhrenverstärker von Du Bridge und Brown[2], den Herr Suzuki hergestellt hatte, durchgefürt.

Die Probe wurde auf einem Ebonitplättchen zwischen die zwei Silberelektroden geschraubt. (Elektrodenabstand rund 7 mm.)

Man bemerkte eine Schwingung des Galvanometers, gleichbeim Anfang der Lichtstrahlung mit einer 100 W Wolframlampe.

(3) Ergebnisse.—a. Die Proben wurden in die Lösung folgender Zusammensetzungen bei Zimmertemperatur für dreißig Minuten eingeweicht.

1. in Wasser.
2. in Goldchloridlösung (0.01% Gew. Au).
3. in Goldrhodanidlösung (0.01% Gew. Au), die aus Goldchlorid und 50-fach überschüssigem Ammoniumrhodanid hergestellt wurde.

Die lichtelektrische Leitfähigkeit dieser Proben nimmt durch solche Behandlungen ab. Der Effekt sit beim 3. Fall stärker als beim 2. Fall. (Fig. 1)

Dieser Einfluß scheint sich mit der Zeit zu verkleinern, wenn man die Proben länger im Dunkeln hält.

b. Man setzt erstens die Proben in gesättigtes Bromwasser, das 10% Kaliumbromid ent-

* Ein Teil von dem Vortrage bei der achten Versammlung dieser Gesellschaft (1955).

1) K. Yamada, S. Oka und T. Mukaibo, *Bull. Soc. Sci. Photo. Japan*, No. 4—5, 1 (1955).

2) Du Bridge und Brown, *Rev. Sci. Instr.*, **4**, 532 (1933).

3) S. Suzuki, *J. Ind. Chem. Japan*, **52**, 77 (1949).

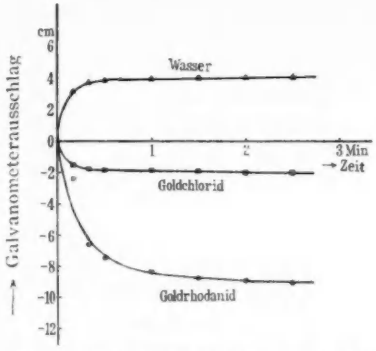

Fig. 1. Der Einfluß von Goldverbindugen.

hält. Diese Proben wurden danach, um das überschüssige Brom abzuscheiden, in die Lösung von 5% Semicarbazid-Chlorwasserstoff, der 10% Kaliumbromid enthält, eingeweicht. Nach wiederholtem Waschen mit distilliertem Wasser, wurde die Behandlung mit Goldrhodanid (a–3) durchgeführt.

Dieses Mal konnte man keine bemerkenswerte Veränderung an der lichtelektrischen Leitfähigkeit herausfinden.

c. Eine sehr kleine Menge von Gold wurde, durch Verdampfung in Vakuum (10^{-3} mmHg), auf die Oberfläche des Kristalls hinzugesetzt[4]).

Die lichtelekrische Leitfähigkeit dieser Proben nimmt aber dadurch sehr stark ab. (Fig. 2)

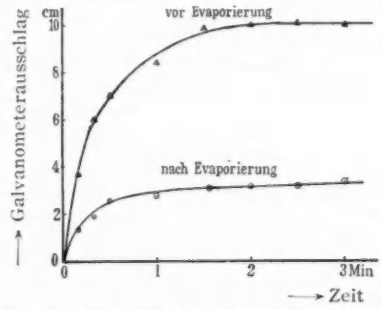

Fig. 2. Der Einfluß von evaporiertem Gold.

d. Statt Gold, wurde eine kleine Menge von Silber auf die Proben hinzugesetzt. Diese Proben wurden dann in die Lösung von Goldrhodanid eingeweicht.

In diesem Fall, war der Einfluß von der Goldverbindung nicht gross.

e. Die beiden nach d. hergestellten Proben wurden wie b mit Bromwasser behandelt.

Dadurch war die Wiederherstellung von der lichtelektrischen Leitfähigkeit bei solchen Proben, welche keine Wirkung von Goldrhodanid erlitten, bemerkenswerter. Die lichtelektrische Leitfähigkeit erniedrigende Wirkung von Silber wurde dagegen durch Bromierung fast vollkommen vernichtet. (Fig. 3)

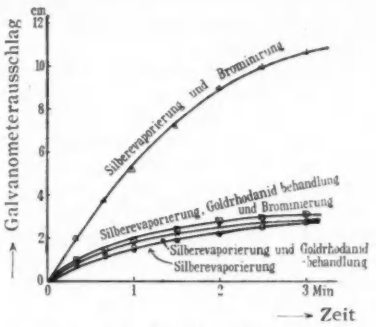

Fig. 3. Der Einfluß von Evaporierung des Silbers, Goldrhodanidbehandlung, und Bromierung.

f. Nach Bromierung wurden die Proben für 2–3 Wochen im Dunkeln gehalten und dann in die Lösung von Goldrhodanid eingesetzt.

In diesem Falle, geschieht, die Verminderung von lichtelektrischer Leitfähigkeit wieder. (Fig. 4)

Fig. 4. Der Einfluß von Goldrhodanid auf die Proben, die nach Bromierung in Dunkel gehalten wurden.

g. Durch Einweichung in die Lösung von Ammoniumrhodanid, dessen Konzentration dieselbe wie von a. ist, beobachtete man keinen so großen Einfluß auf die lichtelektrische Leitfähigkeit, obwohl die Oberfläche dieses Kristalls davon starken Schaden erlitt.

Diskussion

(1) Zur Deutung der Ergebnisse. — Ein Kristall von Silberbromid, der in dem nicht luftdicht verschlossenen Ofen hergestellt wird, ist wegen der Verdampfung von Brom nicht stöchiometrich, sondern enthält überschüssiges Silber. Es ist also wahrscheinlich, daß dieses Silber nahe an der Oberfläche od. in den vielerlei Unvollkommenheiten sehr kleine Silberkeime bildet und durch Gold

4) Die auf das Silberbromid hinzugesetzten Körnchen von einigen Metallen u. s. w. üben auf die lichtelektrische Leitfähigkeit einen bemerkenswerten Einfluss aus (z. B. Cadmiun; heftige Vergrösserung). Untersuchung darüber wird nächstens veröffentlicht).

substituiert wird. Würden unter den Umständen diese Silberkörnchen durch Bromierung verloren gehen, so hätte die Goldvervindung folglich keine ausgezeichnete Wirkung auf die Proben.

Diese Ergebnisse sind also einer der Beweise, daß die Goldsensibilisierung ihre Ursache von diesem Ersatz hat. Auch die Tatsache, daß auf das Silberbromid die zugefügten Goldkörnchen die lichtelektrische Leitfähigkeit erniedrigende Wirkung hat, unterstützt diese Meinung.

Der kleinere Einfluß von dem Ersatz der verdampften Silberkeime durch Gold sollte aus diesem Grund, daß die Wirkung dieser Keime sich nur auf die makroskopische Oberfläche beschränkt, erklärt werden.

Die Proben, die nach Bromierung lange im Dunkeln gehalten wurden, hatten weniger lichtelektrische Leitfähigkeit und zeigten endlich negativen Effekt; Diese Erniedrigung der Leitfähigkeit erlosch durch zweimalige Brominierung. Es ist möglich, daß durch langsame Zersetzung Silberkörnchen verursacht werden, wenn diese Vermutung zutrifft, kann die Wiederholung von Goldeffekt bei solchen Proben leicht verständlich gemacht werden.

Die Reihenfolge von dem Vermögen verschiedener Goldverbindungen stimmt mit dem Sensibilisierungsvermögen überein.

(2) **Mechanismus.**—Die ohenerwähnte lichtelektrische Leitfähigkeit erniedrigende Wirkung von Goldkeimen kann ohne ausführlichere Aufklärung des Lichtempfindungsprozesses nicht ganz klar werden. Aber sie würde nach der bisherigen Lichtempfindungstheorie auf diese Weise erklärt.

Die Austrittsarbeit von Gold bzw. Silber ist;

	optisch	thermisch
Silber	4.73 eV.	4.06
Gold	4.76	4.23

Das Fermische Energieniveau von Silber liegt bei ca. 1 eV. tiefer als das Leitungsband von Silverbromid und Gold befindet sich noch tiefer. Deswegen werden die Goldkeime, wie Hörlin und Müller in ihrem älteren Bericht behaupten[5], stärkere Elektronenfallen als diejenigen aus Silber (Fig. 5). Diese negative Ladung tragenden Keime ziehen Silberionen in Zwischengitterstellen, welche den Hauptteil von Ionenleitung in Silberbromid innehaben aw sich. Die dadurch hervorgerufene heftigere Verminderung an Silberionen, neben der Verminderung an Elektronen, erzeugt eine Abnahme an der lichtelektrischen

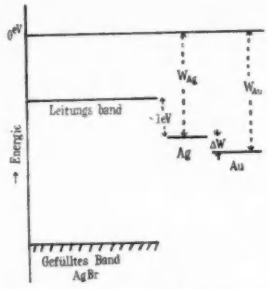

Fig. 5. Energiediagramme.

Leitfähigkeit in dem Falle von Goldzusatz.

Nach der Lichtempfindungstheorie von Mitchell[6], im Gegensatze zu der Theorie von Mott und Gurney[7], sollten diese Goldkeime sich als stärkere Fänger von Elektronendefektstellen beweisen. Aber diese Meßergebnisse können auch nach dieser Theorie verständlich sein, weil bei diesen Umständen eine Aufnahme an den Fänger von Elektronendefektstellen die Entstehung von Silber aus Silberionen dringend verlangen könnte. Die ausführlicheren Gründe, warum diese Goldkeime dabei wirksamer sind, sind noch nicht klar. Aber das stärkere Widerstandsvermögen von Goldkeimen gegen Bromierung kann ihre Haltbarkeit als der Fänger von Elektronendefektstellen zeigen.

Für die Entscheidung dieses Gegenstandes sollten mehrere Untersuchungen erforderlich sein.

Zusammenfassung

1. Die Einflüsse von Goldsensibilisierung auf den elektronischen sowie ionischen Prozeß der Photographischen Lichtempfindung wurden durch die Messung von lichtelektrischer Leitfähigkeit untersucht.

2. Der Zusatz von Gold bzw. Goldverbindungen wurde in den folgenden Weisen durchgeführt;

a. Die Evaporierung von metallischem Gold.

b. Die Einweichung in die Lösung von Goldchlorid bzw. Goldrhodanid.

3. Diese Untersuchung ergab die folgenden Tatsachen;

a. Goldverbindungen sind wirksam nur wenn die Probe Silberkeim enthält.

b. Die Behandlungen mit Goldverbindungen lassen die lichtelektrische Leitfähigkeit des Silberbromides heftig vermindern und rufen oftmals den negativen Effekt hervor.

5) H. Hoerlin und F.W.H. Müller, *J. Opt. Soc. Amer.*, **40**, No. 5, 246 (1950).

6) J.W. Mitchell, *J. Photo. Sci.*, Vol. 1,110 (1953).

7) N.F. Mott und R.W. Gurney, "Electronic Processes in Ionic Crystals", Oxford Clarendon Press, (1940).

4. Die Verfasser dieses Berichtes sind der Ansicht, daß die Silberkeime in od. auf dem Silberbromid durch Gold substituiert wird und diese Goldkeime als die Fänger von Elektronen od. Elektronendefektstellen stärkere Wirkung haben.

Herrn Dozent S. Suzuki in unserem Laboratorium möchten wir für seine Ratschläge unseren herzlichen Dank aussprechen.

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Photonitrosation of Cycloalkanes with Nitrosyl Chloride. I. Synthesis of Cyclohexanone Oxime*

By Yoshikazu Ito

(Received August 29, 1955)

Introduction

It has been reported[1] that nitrosyl chloride reacts with most of the organic compounds and may cause various types of reactions such as nitrosation, chlorination, chloronitrosation, oxydation and diazotization. Of these reactions, nitrosation of hydrocarbons under the influence of light is particularly interesting. This reaction was first investigated by Lynn[2] and Hilton[3] and later by Mitchell and Carson[4]. From their work it was found that aliphatic hydrocarbons, for example, *n*-heptane or *n*-hexane, may be nitrosated by nitrosyl chloride under the influence of light and subsequently isomerized to the corresponding ketoximes. If ketoximes are obtainable from cycloalkanes in this way, this procedure will probably present a new route to prepare cycloalkanone oximes which are important intermediates of polyamide from lactam.

From this point of view, the author has investigated the nitrosation of cycloalkanes with nitrosyl chloride, and, first of all, cyclohexane was used as cycloalkane. From the results of preliminary experiments it was found that cyclohexane is unable to react with nitrosyl chloride at room temperature in the dark, but reacts immediately in the presence of sunlight, forming cyclohexanone oxime. However, this photonitrosation is generally accompanied by various side reactions corresponding to the reaction conditions. Therefore, for the purpose of obtaining cyclohexanone oxime in a good yield, it is necessary to find the optimum conditions under which the side reactions are reduced as far as possible and the rate of photonitrosation is favorably rapid.

Naylor and Anderson[5] reported a similar photonitrosation of cyclohexane, and according to their work, cyclohexanone oxime was obtained in a good yield (at least 71%) by adding nitrosyl chloride slowly and continuously into cyclohexane so that only a slight trace of color was present at any instant, maintaining the reaction liquid at low temperature (−30∼0°C). According to the author's results, it seems that such low temperature (−30∼0°C) and such low concentrations of nitrosyl chloride in cyclohexane, which Naylor proposed for the optimum conditions, may not always be necessary.

The present paper deals with the photonitrosation of cyclohexane with nitrosyl chloride and shows the effects of reaction conditions on the yield of cyclohexanone oxime.

Experimental

Reagents.—Crude cyclohexane obtained by the hydrogenation of pure benzene was purified by treating it with mixed acid (a ratio of sulphuric acid to nitric acid is 1.5:1) and washing it thoroughly with water followed by distillation. Physical constants of such purified cyclohexane are:

b. p. 80.2°C, n_D^{15} 1.4290, d_4^{15} 0.7991.

Nitrosyl chloride was prepared by adding a solution of nitrosyl sulfuric acid in conc. sulfuric acid to dried sodium chloride at 80°C. Pure

* This work was presented in the 6th annual meeting of the Chemical Society of Japan in April, 1953, in Kyoto.

1) L.J. Beckham, W.A. Fessler and M. Kise, *Chem. Rev.*, **48**, 320-96 (1951).

2) E.V. Lynn, *J. Am. Chem. Soc.*, **41**, 368 (1919).

3) E.V. Lynn and Hilton, ibid., **44**, 645 (1922).

4) S. Mitchell and S.C. Carson, *J. Chem. Soc.*, **1936**, 1005.

5) M.A Naylor and A.W. Anderson, *J. Org. Chem.*, **18**, 115-20 (1953).

nitrosyl sulfuric acid was prepared following the method described in a piece of literature[6]. Pure nitrosyl chloride (b. p. −5.5°C) was obtained by condensing crude nitrosyl chloride gas and then rectifing it repeatedly.

Apparatus.—A photoreactor employed for continuous reaction is shown in Fig. 1. One of the most effective and convenient light sources for this reaction was the high vapor pressure mercury lamp of [ca. 2 atm. of which the spectrum is shown in Fig. 3. Another type of photoreactor which is shown in Fig. 2 was also employed for the investigations of reaction conditions.

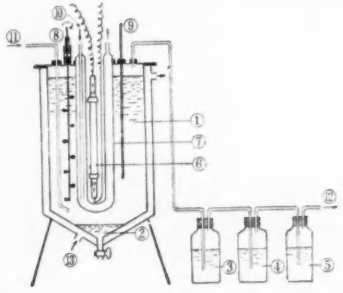

Fig. 1. Photoreactor for continuous reaction.

1. Cyclohexane
2. Oily products
3. Sulphuric acid
4. Aqueous caustic soda
5. Liquid paraffin
6. Mercury lamp
7. Cooling glass tube
8. Stirrer
9. Thermometer
10. Cooling water
11. Gas inlet
12. Gas outlet
13. Brine inlet

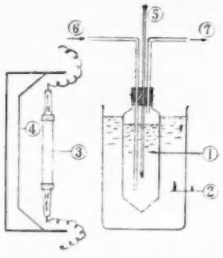

Fig. 2. Photoreactor for batch reaction.

1. Glass reactor
2. Cooling bath
3. Mercury lamp
4. Reflector
5. Thermometer
6. Gas inlet
7. Gas out let

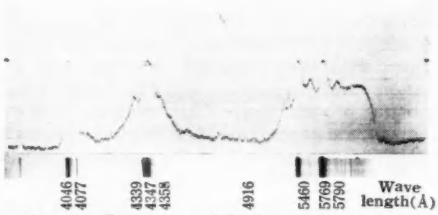

Fig. 3. Spectrum of high vapor pressure mercury lamp.

Procedure.—**(1) Batch Reaction.**—100 ml. of cyclohexane were charged into a reactor (Fig. 2) and nitrosyl chloride was blown into cyclohexane under irradiation. The color of the reaction liquid changed from colorless to cloudy yellow and oily substances began to separate from the reaction liquid. After completion of the addition of nitrosyl chloride, the reaction product was separated from unreacted cyclohexane, dissolved in cold water and then neutralized with 20% aqueous caustic soda until it had pH 6.5. Crystals of precipitated oxime were separated from the mother liquor and dried. Additional amounts of crude oximes were obtained by extracting the latter with cyclohexane. Crude oximes were purified by recrystallization with methanol.

(2) Continuous Reaction.—4.7 l. of cyclohexane were charged into a reaction vessel (Fig. 1) and irradiation was applied with sufficient stirring. A gaseous mixture of nitrosyl chloride

Table I

Effect of temperature

Temperature*	Reaction time	Nitrosyl sulfuric*** acid used	Color of reaction liquid	Pure oxime	Yield****
°C	hr.	g.		g.	%
0**	5	14.1	Yellow	5.36	63.3
5**	5	15.3	Yellow	5.38	63.5
10	5	14.6	Yellow	5.89	65.4
15	5	13.2	Yellow	5.41	63.9
20	5	14.6	Yellow	4.48	52.8
25	5	15.6	Greenish yellow	2.93	37.6
30	5	14.3	Greenish yellow	3.57	44.5

* Temperature was controlled within a range of ±1°C.
** A mixture of cyclohexane and benzene (80 : 20, by volume) was used.
*** Nitrosyl sulfuric acid was used as a solution in conc. sulfuric acid (1 : 1, by weight).
**** The yield is that based on the consumed cyclohexane.

6) Coleman, Lillis and Gohen, "Inorganic Syntheses", (1939), I, p. 55.

and hydrogen chloride was continuously bubbled into cyclohexane at a definite rate. After about thirty minutes, the oily products were withdrawn from the bottom of the vessel and, at the same time, cyclohexane was added through the top inlet. The gases drawn off from the reactor were led in sequence-conc. sulfuric acid, aqueous caustic soda and liquid paraffin. Nitrosyl chloride was caught by sulfuric acid to form nitrosyl sulfuric acid, hydrogen chloride by caustic soda, and cyclohexane by liquid paraffin.

(3) The Identification of Reaction Product.—100 ml. of cyclohexane was placed in a photoreactor (Fig. 2) and irradiated with a mercury lamp. Five grams of nitrosyl chloride together with 2.8 g. of hydrogen chloride were blown into cyclohexane over a period of three hours at 10°C. After about twenty minutes, oily substances began to deposit at the bottom of the reactor, which increased gradually as reaction proceeded. 6.2 g. of this oily produdt was obtained. After treating the product following the method described above, 3.4 g. of purified crystals were obtained, m.p. 88–89°C, which did not depress the melting point of pure cyclohexanone oxime (m.p. 89°C).

TABLE II
EFFECT OF HYDROGEN CHLORIDE

Mol. ratio NOCl : HCl	Oily product obtained	Color of reaction liquid	Pure oxime obtained	Yield of oxime based on added NOCl
	g.		g.	%
1 : 0	4.0	Greenish yellow	2.17	20.9
1 : 0.9	7.1	Yellow	4.16	39.6
1 : 2.7	6.2	Yellow	3.69	35.2
1 : 4.5	8.2	Yellow	3.86	36.8
1 : 6.3	6.9	Yellow	3.79	36.1

(4) Effect of Temperature.—: Consult Table I.

(5) Effect of Hydrogen Chloride.—: Consult Table II.

Note: A 270 W. mercury lamp was used for light source. 6.2 g. of nitrosyl chloride and various amounts of hydrogen chloride were continuously blown into 150 ml. of cyclohexane at 10°C during a period of five hours.

From these results it may be said that hydrogen chloride added to nitrosyl chloride may act not only as a diluent for nitrosyl chloride but also as an accelerator for the formation of oxime hydrochloride.

(6) Flow Rate of Nitrosyl Chloride.—: Consult Table III.

It seemed that side reactions are mainly affected by the concentrations of nitrosyl chloride in the system. The addition rate of nitrosyl chloride should thus be controlled according to the concentration of nitrosyl chloride at every instance. However, it is practically difficult to measure the concentration of nitrosyl chloride quantitatively by analysing the reaction liquid, because of the very low concentration of nitrosyl chloride which favours the yields of the oxime. Since the solution of nitrosyl chloride in cyclohexane has a characteristic color–reddish brown at high concentrations, and yellow or pale yellow at low concentrations–and since the by-products formed in the system are characterized by blue or green color, the concentration of nitrosyl chloride can be inferred conveniently by this change of color.

The addition rate of nitrosyl chloride must be controlled so as to maintain the yellow or pale yellow color for the purpose of the good yield.

(7) The Influence of Water present in Reaction Mixtures.—Here, crude cyclohexane containing small amounts of water was used in order

TABLE III
EFFECT OF FLOW RATE OF NYTROSYL CHLORIDE

Flow rate of NOCl*	Oily product obtained after 5 hr.	Color of reaction liquid	Pure oxime obtained	Yield of oxime based on added NOCl	Yield of oxime based on consumed cyclohexane
g./hr.	g.		g.	%	%
0.63	4.50	Pale yellow	2.22	40.8	53.0
0.97	5.30	Yellow	2.86	34.2	54.0
1.21	7.55	Yellow	4.33	41.2	69.0
1.90	8.40	Deep yellow	4.46	30.9	70.9
3.64	13.60	Brown	6.16	19.8	49.1

* Hydrogen chloride was added to nitrosyl chloride in a mol. ratio of 1 : 1.

TABLE IV
THE INFLUENCE OF WATER PRESENT IN REACTION MIXTURES

Addition of water	NOCl added for 5 hr.	Temperature	Oily product obtained	Color of reaction liquid	Pure oxime	Yield based on added NOCl
	g.	°C	g.		g.	%
None	6.2	10	9.3	Yellow	5.04	48.5
1%	6.2	10	10.0	Yellow	5.70	53.2
None	8.0	25	6.6	Greenish yellow	2.93	21.3
1%	6.7	25	4.0	Greenish yellow	1.10	10.5

to examine the influence of water on the photonitrosation. The results obtained are listed in Table IV. These results show that the photonitrosation is scarcely influenced by the presence of water at 10°C, but much more influenced at 25°C. It may be reasonable to consider that, on account of its very hygroscopic nature, the oxime hydrochloride formed in reaction mixture absorbs even a trace of water present and forms an oily substance which is insoluble in cyclohexane and is fairly stable below 10°C. At 25°C, oxime hydrochloride present in an oily substance, seems to be gradually hydrolized to cyclohexanone oxime and hydroxylamine.

(8) Continuous Reaction.—A continuous reaction was carried out under the favorable conditions which were established for batch reaction (consult Table V).

TABLE V
CONTINUOUS REACTION

Conditions:—	
Temperature	10±1°C
Mol. ratio of NOCl : HCl	1 : 2
Flow rate of NOCl	51.6 g./hr.
Reaction time	10 hr.
Light source	1 kW. high vapor pressure mercury lamp.
Results:—	
Oily product	914 g.
Pure oxime obtained	463 g.
Consumed cyclohexane	520 g.
Unreacted NOCl	124 g.
Yield based on consumed cyclohexane	72.4%
Yield based on reacted NOCl	74.0%

The yields of oxime based on consumed cyclohexane and reacted nitrosyl chloride were 72.4% and 74.0% respectively. Moreover, these yields may be raised considerably by minimizing the loss of cyclohexane and nitrosyl chloride during operation.

Summary

The photonitrosation of cyclohexane with nitrosyl chloride was investigated. It was established that cyclohexanone oxime may be easily produced in good yield (72%) under suitable conditions. The dilution of nitrosyl chloride with hydrogen chloride was most effective for preventing the side reactions, and the photonitrosation of cyclohexane was carried out successsfully at a temperature of 10°C.

The color of the reaction liquid played the role of indicator for a successful photonitrosation; the side reactions seemed not to occur practically so long as the color of the reaction liquid is yellow, and hence, the addition rate of nitrosyl chloride into cyclohexane should be controlled following the color change of reaction liquid.

The author wishes to thank Dr. K. Hoshino and Dr. H. Kobayashi who instructed him in these studies and permitted this publication.

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Dependence of the Exchange Reaction Rate in Catalyst Bed upon the Rate of Feed Gases and the Length of the Bed

By Sadahiro SAKATA and Noriyoshi MORITA

(Received September 12, 1955)

In a recent paper[1] we published a preliminary report of this article. In the present paper other series of experiments concerning chromic oxide catalyst are included and the reexamination of the relation under consideration is made.

Many papers concerning the kinetics of gaseous reactions in flow systems have appeared since the time of Bodenstein[2]. A brief summary of these papers is made by Harris[3]. In addition to these kinetic studies of chemical reactions, transport phenomena occurring in the flow systems have been treated from an engineering standpoint. Colburn and Chilton[4] discussed the mass- and heat-transfer phenomena at the gas-liquid

1) S. Sakata and N. Morita, *Chem. Eng. (Japan)*, **19**, 64 (1955).
2) M. Bodenstein and K. Wolgast, *Z. physik. Chem.*, **61**, 422 (1908).
3) G.M. Harris, *J. Phys. & Colloid Chem.*, **51**, 505 (1947).
4) A.P. Colburn, *Ind. Eng. Chem.*, **22**, 967 (1930); **23**, 910 (1931); T.H. Chilton and A.P. Colburn, ibid., **23**, 913 (1931); A.P. Colburn and W.J. King, ibid., **23**, 919 (1931); T.H. Chilton and A.P. Colburn, ibid., **26**, 1183 (1934); **27**, 255 (1935).

and the gas-solid boundaries, and introduced the concept of the height of a transfer unit, H.T.U. Hurt[5] applied this concept to catalytic reaction and introduced concepts of the height of a reaction unit, H.R.U., and the height of a catalytic unit, H.C.U. For an unpoisoned catalyst surface and for reaction with no volume change, the relation: H.R.U.=H.T.U.+H.C.U., is established. H.T.U. is independent of the nature of catalyst and is slightly influenced by the change of temperature and pressure; it can be calculated by the condition of gas flow. The method of the calculation of this quantity, or the film resistance, and the degree of contribution to H.R.U., or the over-all resistance, have been considered by Hougen[6], and the minimizing methods of film resistance due to transfer of mass have been indicated.

Contrary to the general complexity of kinetics of reactions conducted in flow systems, exchange reaction has very simple properties even when the reaction is conducted in a flow system. The most prominent property of exchange reaction is that during the course of the reaction the chemical concentrations of all components of the system do not change and, therefore, the reaction rate is independent of the progress of the reaction and can be defined only by the mechanism of the reaction. Consider an *exchange reaction*:

$$AX+BX' \longrightarrow AX'+BX, \qquad (1)$$

where X and X′ are the same chemical species (atom or atomic group) and differ only in the fact that X is originally combined with a chemical species A, and X′ is combined with another species B. Assume that for the detection of this exchange reaction, we used, as usual, an isotope of X, i.e. X*, then the *isotopic exchange reaction*:

$$AX+BX^* \longrightarrow AX^*+BX, \qquad (2)$$

is a fraction of the reaction (1), and the fractional percentage is easily seen from a probability calculation, in so far as the isotopic effect is negligible. Now we denote the rate of reaction (1) by R, number of exchange per sec. per cc. of reactor. Then this exchange reaction rate, R, which is differential in its nature but which can be measured by integral conversion of the isotopic exchange reaction (2), is independent not only of the duration of the reaction, but also of the volume or the shape of the catalyst bed so long as the over-all resistance of the reaction remains constant. In other words, when R changes with any one of the following variations: the feed rate F cc. (S.C.)/sec., reactor diameter D cm., height of the bed Z cm., and the volume of the catalyst $(1/4)\pi D^2 Z$, while the temperature remains constant, then the change shows that any one of the steps of the reaction has been influenced by that variation. When the reaction is catalytic, then so long as the intrinsic catalytic activity remains constant, the change in R indicates some change in mass-transfer steps.

In addition to this prominent feature of exchange reaction, isotopic exchange reaction has two other characteristics. The one is that the heat of reaction is nearly zero, and the other is that the integral rate is expressed by the first order equation. These characteristics are amenable to the kinetic study of chemical reaction.

Anticipating these characteristics, we have studied the catalytic exchange reaction of oxygen atoms between gaseous oxygen and water vapor by use of heavy oxygen. By using chromic oxide catalyst, values of R were measured at varying temperatures by varying the feed rate of reacting gases and the length of the catalyst bed.

Rate Equation

One of the authors in an earlier paper[7] introduced a mathematical relation between the percentage exchange and the gas flow rate, as concerned with the catalytic exchange reaction of oxygen atoms between gaseous oxygen and water vapor on the surface of solid catalyst. There it was ascertained that the exchange reaction rate was related by a simple probability relation to the rate of isotopic exchange reaction regardless of which step of the reaction (viz. adsorption, desorption, surface reaction, or any mass-transfer process) was rate controlling, so long as isotopic effect was negligible, and the following relation was obtained,

$$R'=\{N_A N_B/(N_A+N_B)\}(1/t)\{-\ln(1-x)\} \qquad (3)$$

Here, N_A and N_B are the total numbers of molecules of chemical species AX+AX* and BX+BX* in a unit volume of feed gases at S.C. and remain constant during the exchange reaction, x is the conversion represented by the net fraction of isotopic exchange to equilibrium, and t is the contact time in sec. R' denotes the rate of the exchange reaction concerning per unit volume of the reacting gases at S.C. and is related

5) D.M. Hurt, ibid., 35, 522 (1943).

6) B.W. Gamson, G. Thodos and O.A. Hougen, *Trans. Am. Inst. Chem. Eng.*, 39, 1 (1943); O.A. Hougen and K.M. Watson, *Ind. Eng. Chem.*, 35, 529 (1943); K.H. Young and O.A. Hougen, *Chem. Eng. Progr.*, 46, 146 (1950); O.A. Hougen, *Z. Electrochem.*, 59, 479 (1953).

7) N. Morita, This Bulletin, 15, 166 (1940).

with R by the relation: $R=R'F_e(273/T)\ (p/760)$, where F_e is the void fraction of the catalyst bed and T and p are the temperatures in °K and pressure in mmHg. The time of contact can be expressed by: $t=(\pi D^2 Z F_e/4F)\ (237/T)\ (p/760)$, and therefore Eq. (3) becomes:

$$R=(4F/\pi D^2 Z)\{N_A N_B/(N_A+N_B)\}\{-\ln(1-x)\}. \quad (4)$$

Norris[8] contemplated the rate equation deduced by Duffield and Calvin[9] as identical with Eq. (3), and set forth his opinion concerning the application of the equation for heterogeneous reactions. Harris[10] also introduced the same kind of equation for isotopic exchange reactions and deduced equations dealing with the kinetic implication of isotopic effect. For oxygen isotopes, isotopic effect is not large and we will not consider it in this paper.

In addition to the rate equation deduced above, we can point out the following interesting relation:

$$\text{N. R. U.}=\int_{u_A}^{u_{Ao}} \frac{du_A}{u_A-u_{Ae}}=\ln\left(\frac{u_{Ao}-u_{Ae}}{u_A-u_{Ae}}\right)$$
$$=-\ln(1-x) \quad (5)$$

or, $$\text{H. R. U.}=Z/(\text{N. R. U})=Z/\{-\ln(1-x)\}, \quad (6)$$

where u_A is the fraction of AX^* in N_A, and u_{Ao} and u_{Ae} denote the original and equilibrium values of u_A, respectively. By this relation we can calculate H. R. U. from the conversion x. H. T. U. can be calculated from the conditions of the flow of reacting gases in the reactor by Hougen's method or introduced others, and then we can find the percentage contribution of mass-transfer process for the over-all reaction velocity.

Experimental Procedure

Four kinds of quartz tubes were used as the reactor, of which two were vertical and two were horizontal. We call these tubes V–I, V–II, H–I and H–II, respectively, whose dimensions are shown in Tables I–IV. Centered in thereact or is a thin tube of quartz for thermocouple. Pelleted catalyst is poured into the reactor to a fixed height and both ends are filled with granular quartz. The reactor is heated in a properly fitted electrical oven.

Oxygen in cylinder is used as the reacting gaseous oxygen; the content in heavy oxygen was analyzed in advance. The oxygen passes through pressure regulator, flow rate regulator, flow meter, and preheater, and then flows into mixer with water vapor. Heavy oxygen water prepared by fractional distillation of water is placed in a glass cylinder with graduation and pressed with the same pressure used for gaseous oxygen. The water flows at a known speed through the flow rate regulator and flows into evaporator. The evaporator is made of quartz and heated by three small gas burners. The vapor mixes with gaseous oxygen, passes through another preheator, and flows into the reactor. The gaseous mixture from the reactor is passed through condenser. The condensed water is refined as usual[11] and its heavy oxygen content is determined from its excess density as compared with normal water. Comparing the heavy oxygen content with original concentration the conver sion x is determined.

Chromium oxide is prepared from recrystallized chromium alum. The precipitated hydroxide of chromium with ammonia is repeatedly washed with water until no sulphuric acid ion is detectable. The hydroxide is dried in an electrical air oven and then powdered. One part of this powder is throughly mixed with three parts of the "Naegi" kaolin and a small quantity of water is added. The paste is pressed out of a press made of brass, having several pores of 2 mm. dia. in the bottom, and then cut into 2 mm. lengths. The pellete are first air-dried and then placed in an electrical oven at 110°C, and finally dried at 500°C for 7 hr. under oxygen gas stream. Before each experiment, a reacting gas mixture is passed through the catalyst for several ten-minute periods after which we can expect the steady state of the exchange reaction.

Results obtained

Tables I–IV show the results obtained under various conditions of experiments. In these tables A is the cross sectional area of the reactor and α is the volume ratio of gaseous oxygen to water vapor. Experimental number show the order of experiments. Throughout all the experiments the

TABLE I

DATA OBTAINED BY V–I (RUN 600)

D=1.6 cm., A=2.01 cm², Z=24.0 cm. (No. 1–19): 23.5 cm. (No. 29–36); 23.8 cm. (No. 37–51)

Exp. No.	Temp. °C	F/A cc./sec.·cm²	α	x	$R\times10^{-18}$ atoms/sec.·cc.	H. R. U. cm.
632	542	16.5	2.28	.789	7.34	15.1
611	538	15.0	2.14	.823	7.49	13.9
636	522	16.4	2.38	.605	4.10	25.3
629	501	17.3	2.06	.432	2.96	41.5
602	489	15.2	2.05	.405	2.32	46.3
633	488	17.1	2.07	.375	2.42	50.0
631	541	23.0	2.19	.652	7.13	22.3
613	540	22.3	2.18	.729	8.35	18.3
635	522	22.8	2.18	.490	4.51	34.9
630	500	23.6	2.01	.312	2.70	62.9
614	492	22.6	2.11	.321	2.54	62.1
634	487	23.8	1.99	.233	1.93	88.8
645	563	32.0	2.08	.895	21.29	10.6

8) T.H. Norris, *J. Phys. & Colloid Chem.*, **54**, 777 (1950).

9) R.B. Duffield and M. Calvin, *J. Am., Chem. Soc.*, **68**, 557 (1946).

10) G.M. Harris, *Trans. Faraday Soc.*, **57**, 716 (1951).

11) T. Titani and N. Morita, This Bulletin, **13**, 409 (1938).

Exp. No.	Temp. °C	F/A cc./sec.·cm²	α	x	$R\times10^{-18}$ atoms/sec.·cc.	H.R.U. cm.
640	542	32.1	2.02	.717	12.15	18.9
610	537	35.2	2.21	.653	10.60	22.7
651	522	33.7	1.81	.381	5.09	49.7
648	501	32.0	2.33	.339	3.69	57.5
601	494	34.7	2.20	.366	4.49	52.9
642	561	37.7	2.61	.844	18.39	12.8
646	560	40.7	2.21	.856	22.62	12.3
639	539	39.2	2.18	.590	10.08	26.7
650	533	42.6	2.00	.506	9.03	33.8
643	523	38.7	2.37	.581	9.31	27.3
638	503	38.1	2.42	.286	3.51	70.7
604	598	64.8	2.49	.931	46.53	8.9
617	580	47.5	2.28	.890	29.36	10.9
619	556	49.4	2.03	.634	14.72	23.9
612	554	60.7	2.08	.558	14.51	29.4
616	500	48.9	2.22	.227	3.57	93.5
603	492	67.7	2.30	.183	3.81	119

TABLE II

DATA OBTAINED BY V–II (RUN 700)

$D=2.5$ cm., $A=4.9$ cm², $Z=6.0$ cm.

Exp. No.	Temp. °C	F/A cc./sec.·cm²	α	x	$R\times10^{-18}$ atoms/sec.·cc.	H.R.U. cm.
702	475	0.43	2.00	.652	0.539	5.7
704	425	〃	〃	.197	.112	27.4
703	400	〃	〃	.145	.080	38.2
712	475	0.46	2.00	.555	0.444	7.4
707	450	〃	〃	.450	.328	10.0
714	425	〃	〃	.210	.129	25.5
713	400	〃	〃	.161	.096	34.3
710	500	1.50	2.00	.524	1.327	8.1
708	475	〃	〃	.278	0.581	18.5
716	475	〃	〃	.231	.470	22.9
715	450	〃	〃	.111	.210	51.3

TABLE III

DATA OBTAINED BY H-I (RUNS 100–500)

$D=1.6$ cm., $A=2.01$ cm², $Z=30.0$ cm.

Exp. No.	Temp. °C	F/A cc./sec.·cm²	α	x	$R\times10^{-18}$ atoms/sec.·cc.	H.R.U. cm.
107	590	34.7	2.27	.894	17.61	13.3
503	580	43.9	1.92	.945	31.00	10.3
105	540	44.2	2.06	.670	11.54	27.1
210	535	33.4	2.57	.729	9.09	23.0
109	520	35.8	2.21	.404	4.25	57.9
405	520	42.1	2.10	.442	5.73	51.5
207	495	44.1	2.03	.374	4.89	64.2
110	480	35.4	2.11	.185	1.69	141
301	470	34.9	1.92	.196	1.86	137
111	445	35.7	2.05	.085	0.76	333
205	438	44.6	1.94	.099	1.12	289
103	580	62.0	1.95	.924	38.50	11.6
106	580	47.8	1.82	.845	22.21	16.1
504	570	57.0	2.23	.959	41.34	9.4
502	530	52.5	2.79	.643	10.68	29.2
108	520	49.5	1.56	.596	11.90	33.1
208	506	63.0	1.81	.409	8.26	57.1
508	505	55.2	2.40	.460	7.37	48.6
507	500	45.3	1.72	.398	5.85	59.1
201	480	52.2	3.06	.189	4.32	69.0
505	450	57.8	2.06	.261	8.36	50.0

TABLE IV

DATA OBTAINED BY H–II (RUN 000)

$D=1.7$ cm., $A=2.27$ cm², $Z=3.0$ cm. (No. 002–013); 2.1 cm. (No. 0.17–021)

Exp. No.	Temp. °C	F/A cc./sec.·cm²	α	x	$R\times10^{-13}$ atoms/sec.·cc.	H.R.T. cm.
013	500	0.44	2.00	.791	1.649	1.9
004	475	〃	〃	.535	0.807	3.9
003	450	〃	〃	.346	0.446	7.1
005	425	〃	〃	.271	0.332	9.5
002	400	〃	〃	.113	0.126	25.0
021	724	46.1	1.68	.624	166.1	1.5
020	693	46.5	1.64	.446	111.8	2.0
018	653	45.9	1.70	.234	57.7	3.9
017	598	45.9	1.70	.068	20.1	13.5

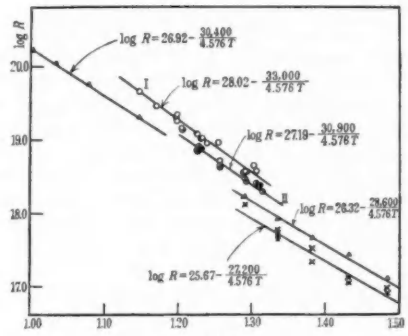

Fig. 1. Exchange reactions of oxygen atoms.

△ Run 000

◑ Run 600 $F/A\leq23.8$ cc.(s.c.)/sec.·cm².

○ 〃 〃 ≥32.0

× Run 700

same catalyst was used repeatedly, having been only treated with oxygen gas at 500°C before each run. During these runs the catalytic activity had remained almost constant, as will be shown later.

In Fig. 1 the points indicated by circles are the relations of $\log R$ vs. $1/T$ obtained by run 600. The fluctuation of each experimental point is rather large and the effect of the differences in linear velocity of reacting gas mixture F/A on the rate R can not be confirmed point-by-point. But, generally speaking, these points show a tendency toward a smaller R with decreasing gas velocity. When, for convenience, we classify these points into two groups, one with a feed rate larger than 32.0 and the other with one smaller than 23.8 cc. (S. C.)/sec.·cm², then we can draw the two lines I and II in Fig. 1. The ratio in R for the two lines ranges from 1.3 to 1.5. These differences can be attributed only to the differences in the flow

velocities of reacting gases. The mean value of α is 2.18, most of the values deviating not more than $\pm 5\%$, although the maximum deviation is about 20%. The effect of α on R was examined in an other run of experiments not included in this paper, and it was ascertained that these deviations in α had no effect on the rate R.

The results obtained by runs 000 and 700 are represented by triangles and crosses, resp. (Fig. 1), where the shorter catalyst beds and smaller feed rates were applied. The decreases in R are more conspicuous than those in line-II, and at run 700 the values of R are about one-fourth the values in line-I.

The runs 100–500 are conducted in a horizontal reactor and differ slightly from run 600 in the length of the catalyst bed. Deviation from linearity of the experimental results (not shown in Fig. 1) is more marked than in run 600. As runs 100–500 were the preliminary experiments done at high feed rates, and, in addition, as the reactor was horizontal and channeling was conceivable, thus a larger experimental error may have resulted. Taking this fact into consideration, the coincid ence with run 600 is considerable, indicating that during all the runs the catalytic activity remained almost constant.

Discussion

As noted in Fig. 1, the activation energy of the exchange reaction ranges from 33.3 to 27.2 kcal./equiv. These high values of activation energy indicate that the mass-transfer processes can not be the main controlling factor of the reaction. The values of the frequency factor also show that the internal surface of the catalyst plays a dominant role. The value ranges from 1×10^{28} to 5×10^{25}. The outer-surface area a_v of the catalyst pellets is 21.6 cm²/cc. and the collision frequency of the water molecules on this surface is 1.26×10^{24} molecules/sec.·cc. under the operating conditions of 500°C and 1/3.2 atm. The frequency factor is about 8,000–40 times greater than this collision frequency.

Although the mass-transter can not be the rate-controlling step, the decrease in linear velocity of reacting gas mixture and the shortening of the bed length retard the over-all rate R to a significant extent. Decrease in R accompanies the decrease in both activation energy and frequency factor. This fact clearly indicates that the mass-transfer processes have influence on the over-all rate to some extent.

The relative importance of film resistance to the rate R can be seen by calculating H. T. U. From the observed values of the pellet density of the catalyst 1.02 g./cc. and the bulk density of the catalyst bed 0.735 g./cc., and from the data cited in preceeding sections, we have calculated H. T. U. by Hougen's method. In Table V, the mass

TABLE V

CONTRIBUTION OF MASS-TRANSFER

Exp. No.	Temp. °C	$G\times10^2$ g./sec.·cm²	$\mu_m\times10^4$ g./sec.·cm.	D_m cm²/sec.	H. T. U. cm.	H. T. U. / H. R. U. ×100
021	724	5.51	4.28	1.265	.151	10.33
017	598	5.49	3.83	1.033	.155	1.15
013	500	0.054	3.61	0.864	.015	0.79
002	400	0.054	3.27	0.702	.015	0.06
103	580	7.54	3.87	1.000	.182	1.57
210	535	4.18	3.73	0.922	.134	0.58
507	500	5.43	3.56	0.864	.158	0.27
604	598	8.11	4.00	1.032	.185	2.07
645	563	3.93	3.84	0.972	.131	1.24
632	542	2.04	3.80	0.933	.094	0.62
648	501	3.97	3.67	0.864	.133	0.23
603	492	8.39	3.63	0.850	.194	0.16
710	500	0.183	3.61	0.864	.028	0.34
702	475	0.052	3.51	0.820	.015	0.24
715	450	0.183	3.43	0.780	.028	0.05
703	400	0.052	3.27	0.702	.015	0.04

velocity G, mean diffusivity D_m and mean viscosity μ_m are calculated from the temperature, volume velocity and mixing ratio of the gas mixture. From these values the j_d factors are calculated by $j_d=1.82(D_pG/\mu_m)^{-0.51}$, and then H. T. U. by $\text{H. T. U.}=(1/a_v j_d)(\mu_m/\rho D_m)^{2/3}$, where D_p is the effective diameter of the catalyst pellet and is equal to $0.2\sqrt{1.5}=0.245$ cm., and ρ is the density of the reacting gas mixture. From Table V it can be seen that even at the highest temperature in the experiments H. T. U. is 10% of H. R. U., in most cases only one percent or a fraction. The correctness of these calculations is not certified for such flow systems with small Reynolds numbers, but film resistance seems insufficient to explain the retardation of the rate caused by the slowing down of the gas flow.

As long as the intrinsic catalytic activity remains constant, uniform packing of catalyst and piston-like flow of reacting gases will give the largest value of R and any deviation from these conditions always reduces the rate R. Thus non-uniform gas flow, channeling, local eddy motion, convective circulation, longitudinal diffusion of isotopic components, and other disturbances always have retarding effects on R. If we assume that the reaction was conducted under complete mixing of the reacting gases as if it were in a tank reactor, then the observed rate R for high conversion and small flow

rate would be as small as one-third compared with the rate when the reaction was conducted under piston flow.

Hitherto we did not consider the effect of pressure drop through the reactor. Eq. (4) does not contain pressure p. This is due to the fact that the calculations of N_A+N_B and of F are made at the same pressure (i.e. 1 atm). However, the change in pressure will affect the state of adsorption, collision frequency and other stages, and may ultimately affect the intrinsic catalytic activity or other factors governing the rate. Though this is the case, yet the highest value of the pressure drop is about 120 mmHg and the mean pressure throughout the reactor, 760+60 mmHg, is only 8% greater than the normal value. This small deviation will not cause any serious error in the results.

For comparison with our results, we have calculated the rate of exchange reaction between hydrogen and deuterium catalyzed by zins oxide by using Holm and Blue's data[12]. In this case R can be calculated by the equation, again neglecting isotopic effect: $R=(N/2)(S.V.)\cdot\{-\ln(1-x)\}$, where N is the total number of molecules of hydrogen and deuterium in a unit volume. Applying this equation to the data of Table V of Holm and Blue's paper, we have obtained the relation of $\log R$ vs. $1/T$ as shown in Fig. 2.

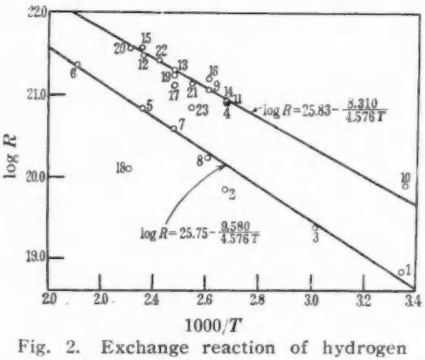

Fig. 2. Exchange reaction of hydrogen atoms (Holm, Blue).

Here the numbers affixed to the experimental points are the order of their data in the mentioned Table. From Fig. 2 we can observe that all the points except Nos. 4, 9, 18 and 23 are almost in linear relation with $1/T$ and that there is no speciality as indicated by the signs b and c in their table. The fact that the points can be divided in two groups: one with lower $S.V.$ and the other with higher $S.V.$ is in qualitative coincidence with our results. But the difference in R in their two groups is about ten and this difference is greater than ours. For hydrogen, isotopic effect may contribute a large effect on the velocity of isotopic exchange reaction and the calculated values of R may be incorrect in absolute value, but the error will not change greatly the mutual relation of these values. As they used a very small quantity of catalyst, the turbulence of reacting gases at the inlet and outlet may have contributed a considerable percentage. In addition, it is not certain to what extent the intrinsic catalytic activity remains constant during the run. These facts make any quantitative comparison difficult.

12) V.C.F. Holm and R.W. Blue, *Ind. Eng. Chem.*, 44, 107 (1952).

Summary

(1) Exchange reaction has the prominent feature that the rate does not change with the progress of the reaction and can be determined only by the mechanism of the reaction. Therefore we can immediately detect the effect of variation in any one of the reacting conditions by the observed conversion of the isotopic exchange reaction.

(2) The relation between exchange reaction and isotopic exchange reaction is considered and an equation which gives the exchange reaction rate (R) using the integral conversion of the isotopic exchange reaction (x) is introduced.

(3) The method is applied to the exchange reaction of oxygen atoms between gaseous oxygen and water vapor catalyzed by chromic oxide, and examination is made of the effect of the variation in the rate of feed gases and in the length of the catalyst bed.

(4) At feed rates higher than 32.0 cc. (S.C.)/sec. cm^2 the value R remains almost constant, but by the lowering of the feed rate more than this and by the shortening of the bed length, R is decreased. This decrease accompanied decreases both in activation energy and in frequency factor.

(5) The results are explained by the effects of mass-transfer through the gas film, of eddy or diffusional mixing of the reacting gases and of other kinds of disturbances. Mass-transfer resistance of the gas film is a small fraction of the retardation. Mixing of the reacting gases may contribute a higher percent.

(6) The results are compared with the rate of exchange between hydrogen and deuterium measured by Holm and Blue.

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On the Lower Boiling Product of Silicon-methylchloride Reaction

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Among the products obtained from the reaction of silicon and methylchloride, methyltrichlorosilane, dimethyldichlorosilane and trimethylchlorosilane were well known since the finding of the "direct method of synthesis" by Rochow. These three main chlorosilanes have a close boiling point centering around 65°C and have been used for the starting materials of "silicones".

Now we wish to report on the presence of tetramethylsilane $(CH_3)_4Si$ (I'), dimethylchlorosilane $(CH_3)_2SiHCl$ (II') and methyldichlorosilane CH_3SiHCl_2 (III') and a small amount of trichlorosilane $HSiCl_3$ (IV') in the lower boiling product centering around 35°C of the direct synthesis. The compounds (I')[1,2], (III')[3] and (IV')[4,5] have already been characterized, but on the compound (II') only the boiling point has been assumed by calculation to be 35.5°C[6] and 39.1°C[7].

To obtain pure (II'), the starting material was twice distilled through a modified large Stedman column of about 15 theoretical plates and divided into many fractions. These fractions may be roughly included into three main fractions A (b. p. 26°–34°C), B (b. p. 34°–36°C) and C (b. p. 36°–41°C). As the fraction B was supposed to be a plateau of impure (II'), B was repeatedly fractionated through a more efficient column. Finally a constant boiling fraction was obtained, but its chlorine content was found to be lower than the calculated value. The reason may be explained by assuming the contamination of a hydrocarbon by-product having the boiling point close to (II'). In fact, the presence of such a hydrocarbon in the starting material has been found by hydrolysis. Referring to the case of trimethylchlorosilane[8], it may be considered that an azeotrope of (II') and the hydrocarbon is formed at the constant boiling plateau at 34.5°–35°C, but it could not be verified in this experiment.

As it was difficult to separate (II') from the contaminating hydrocarbon by distillation, B was ethanolyzed in excess ethanol and dimethylaniline, and the dimethylethoxysilane thus formed was reacted in a bomb with benzoylchloride. From the product the freaction boiling at 36°C was confirmed to be (II').

Ethanolysis of the fraction B in excess dimethylaniline and ethanol, liberated dimethylethoxysilane, methyldiethoxysilane and a small amount of dimethyldiethoxysilane and ill-defined triethoxysilane. It was supposed that dimethyldiethoxysilane was produced by the fission of Si-H during the course of ethanolysis. The presence of triethoxysilane reveals the presence of (IV') in the redistilled product, this assumption was further supported by the fact that on repeated fractionation of B, the fraction B' having a higher chlorine content was found in front of the plateau B'' as shown in Fig. 1.

By hydrolysis, methylhydropolysiloxanes were obtained as the main product. In this paper, to denote various methylpolysiloxanes, shorthand notation is used which is based on that of Wilcock[9], in which **M**, **D** and **T** represent mono-, di- and tri- functional units. Prime is used to indicate the hydrogen atom directly attached to silicon atom.

Unit	Formula
M'	$(CH_3)_2HSiO_{1/2}$
D'	CH_3HSiO
D	$(CH_3)_2SiO$
T	$CH_3SiO_{3/2}$

The following compounds were made by hydrolyzing the starting material and rigorously distilling the resultant oil.

$\mathbf{M'D'_nM'}$	$(n=0\text{–}6)$
$\mathbf{M'D_nM'}$	$(n=1\text{–}2)$
$\mathbf{D'_n}$	$(n=4\text{–}\ )$
M'D'DM'	

The main components of the resultant oil were a series of linear copolymers $\mathbf{M'D'_nM'}$,

1) J.G. Aston, R.M. Kennedy and G.H. Messerly, *J. Am. Chem. Soc.*, **63**, 2343 (1941).
2) A.P. Mills and C.A. MacKenzie, ibid., **76**, 2672 (1954).
3) R.O. Sauer, W.J. Scheiber and S.D. Brewer, ibid., **68**, 962 (1946).
4) H.S. Booth and W.D. Stillwell, ibid., **56**, 1529 (1934).
5) A. Stock and F. Zeidler, *Ber.*, **56** B, 986 (1923).
6) C.A. MacKenzie, A.P. Mills and J.M. Scott, *J. Am. Chem. Soc.*, **72**, 2032 (1950).
7) R.N. Lewis and A.E. Newkirk, ibid., **69**, 701 (1947).
8) R.O. Sauer, W.J. Scheiber and E.M. Hadsell, ibid., **70**, 4254 (1948).
9) D.F. Wilcock, ibid., **69**, 477 (1947).

which were formed from (II′) and (III′). A small amount of $M'D_nM'$, in which only M′DM′ was accurately characterized, may be assumed to be formed by the fission of Si-H bond during the hydrolysis in the concentrated hydrogen chloride solution.

$$3H(CH_3)_2SiCl+2H_2O = H(CH_3)_2SiOSi(CH_3)_2OSi(CH_3)_2H+3HCl+H_2$$
(M′DM′)

Such a reaction may occur also with Si-H of methyldichlorosilane to form M'_3T, an isomer of M′D′DM′. But in this experiment, the presence of this compound could not be detected accurately. The presence of D'_n, which has already been characterized by Sauer[3] by hydrolyzing (III′), was found between the plateaus of $M'D'_nM'$.

The distribution of these polymers, tetramethylsilane (I′) and hydrocarbon by-product in the hydrolyzates with regard to the chlorine content of the redistilled chlorosilane, is shown in Fig. 2. The properties of these polymers are given in Table II.

Experimental

Starting Materials.—The industrial low boiling methylchlorosilane, having the boiling point between 26°C to 40°C (hydrolyzable chlorine, 40%) obtained from the reaction of silicon and methylchloride was supplied from the Shin-etsu Chem. Ind. Co.

A. Chlorosilane and Its Ethanolysis

Distillation.—The starting material (4 Kg.) was fractionated through a modified Stedman column of about 15 theoretical plates (38 mm. inner diameter, packed length 30 cm.). From the boiling point and the chlorine content, the distillates were roughly separated into three main fractions as follows.

Main fraction	Boiling point (°C)	Hydrolyzable chlorine (%)	Weight (%)
A	26–34	–36	25
B	34–36	36–43	25
C	36–41	43–60	50

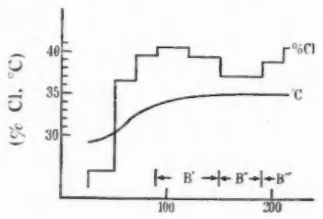

Fig. 1. Redistillation of fraction B through a 30 plates column.

As the fraction B was supposed to be an incomplete plateau, a part of which was fractionated through a Stedman column of about 30 theoretical plates (inner diameter 18 mm. and packed length 40 cm.). The result are shown in Fig. 1.

The distillation curve obtained was similar to that of the starting material, but the chlorine content of the distillate was somewhat different. The fraction B″ having a slightly lower chlorine content than the neighbouring fractions, B′ and B‴, was found. The higher values in B′ and B‴ were supposed to be caused by the contamination of a asmall amount of trichlorosilane (IV′) (b.p. 31.5°C[4], 31.8°C[5]) Calcd. Cl, 78.5%) and methyldichlorosilane (III′) (b.p. 41.0°C[3]) Calcd. Cl, 61.5%), respectively. The fraction B″ (Found Cl, 37.1%) was distilled through the same column and the constant boiling frection of 34.5° to 35°C was obtained, but the chlorine contents of 39.4, 35.1 and 36.4% were found with the amount of each 10 cc. of the distillate. If the fraction B″ was (II′) contaminated only by a small amount of (IV′) and (III′), the redistilled fraction having the minimum chlorine content would become closer to the chlorine content calculated for (II′) (37.4%). In this experiment, the second fraction having the minimum chlorine content (35.1%) did not close to the calculated value, but too small a value resulted.

Ethanolysis.—A fraction of B (150 g., b.p. 35°–36°C, Anal. Cl, 42.5%) was added to the mixture of excess of ethanol (120 g.) and dimethylaniline (250 g.) in a three-necked flask equipped with an efficient stirrer, a dropping funnel and a condenser with a calcium chloride tube. During the reaction, the mixture was cooled with an ice-bath below 5°C. After the addition of the chlorosilane, the reaction mixture was refluxed over a period of two hours with vigorous stirring, followed by the separation of dimethylanilinehydrochloride through a separating funnel and the fractional distillation of the organic layer. The fraction boiling at 53°–57°C (39 g.) thus obtained, was rigorously fractionated by a Stedman column of about 50 theoretical plates. The fraction boiling at 54°C was found to be dimethylethoxysilane $H(CH_3)_2SiOC_2H_5$ from the analysis of H(-Si). n_D^{20}, 1.3683, d_4^{20} 0.7572, MR_D Found: 31.00, Calcd.[10]: 31.30.

Anal. Found: H(-Si), 0.94%. Calcd. for $H(CH_3)_2SiOC_2H_5$: H(-Si), 0.97%.

This compound contained a trace of chlorine compound detectable by the Beilstein test and gradually decomposed by evolving a gas from the bottom of the receiver. Even after repeated distillation, the chlorine compound and evolution of the gas did not completely disappear.

The higher boiling fraction collected from several ethanolysis reactions, was fractionally distilled through a Stedman column of about 30 plates. The following three ethoxysilanes were obtained.

Methyldiethoxysilane, $HCH_3Si(OC_2H_5)_2$.

b.p. 97.5°C, n_D^{20} 1.3772

10) Calculated from bond refractivities by E.L. Warrick, *J. Am. Chem. Soc.*, **68**, 2455 (1946).

Reported[11]: b.p. 97.5°C, n_D^{25} 1.3738, d_{25}^{25} 0.8295

Dimethyldiethoxysilane, $(CH_3)_2Si(OC_2H_5)_2$.

b.p. 112°C, n_D^{20} 1.3821, d_4^{20} 0.8398

MR_D Found: 41.09, Calcd.[10]: 41.06

Reported[12]: b.p. 114°C, n_D^{20} 1.3805, d_4^{20} 0.8395

Triethoxysilane, $HSi(OC_2H_5)_3$.

b. p. 134°–5°C, n_D^{20} 1.3840

Anal. Found: H(-Si), 0.43%, Calcd. 0.61%

Reported[6]: b.p. 131.5°C, n_D^{20} 1.3767

The data of triethoxysilane did not accord well with the reported value. On account of the small amount (1 cc.) of this fraction, the satisfactory separation from the neighbouring compounds could not be achieved. By the alcoholysis reaction carried out as above, cyclocompound $\mathbf{D}_4'$ (Reported[3]: b.p. 134.5°C, n_D^{20} 1.3873) having the boiling point close to that of triethoxysilane might not be formed. The active hydrogen content of this fraction lower than the calculated value also reveals the absence of $\mathbf{D}_4'$ (Calcd. H(-Si), 1.68%).

Chlorination of Dimethylethoxysilane.—Dimethylethoxysilane (28 g., 0.27 mol.) was reacted with benzoylchloride (38 g., 0.27 mol.) in an iron bomb at 200°C over a period of four hours. The reaction mixture was rigorously fractionated through a Stedman column of about 50 theoretiplates. The constant boiling fraction at 36°C (2 cc.) was obtained. From its chlorine content, it was found to be dimethylchlorosilane (II'). n_D^{20} 1.3820

Anal. Found: Cl, 37.6%. Calcd. for (II'): Cl. 37.4%.

B. Hydrlyzates

Hydrolysis.—Hydrolysis was carried out by adding a sufficient amount of cracked ice to the ice-cooled chlorosilane. The oily layer was vigorously shaken with fresh ice-water repeatedly, but it was found to be difficult to complete the hydrolysis, for the red color of methylorange, which was added as an indicator, appeared gradually on standing. To complete the hydrolysis the hydrolyzate and water were vigorously stirred at room temperature with an efficient stirrer. When the red color of methylorange appeared, the mixture was titrated back to the orange color with a dilute sodium bicarbonate solution until the orange color remained unchanged. Then useing chlorophenolred (pH 5.0–6.6) as an indicator, the same treatment was repeated. The hydrolysis reaction was very slow and it required twenty to thirty hours' stirring with 200 to 250 g. of the hydrolyzate. The hydrolyzates of the starting material and fraction A, which contain volatile tetramethylsilane (I'), were twice washed with fresh ice-water, followed by the dehydration on sodium sulfate and the fractionation to distil off (I'). And the residue was neutralized as above.

In spite of these careful treatments, a trace of chlorine compound was sometimes found in the distillate. Accordingly, on each fractionation, the distillate and the residue were tested by the Beilstein test and a trace of chlorine compound was again hydrolyzed off.

Composition of the Hydrolyzate.—As it was very difficult to separate the starting material into its components through distillation, the hydrolysis was carried out with the representative fractions which were obtained by redistillation through the 15 plate large Stedman column. The results are given in Table I (Expt. 1 to 8).

TABLE I

HYDROLYSIS OF REDISTILLED AND STARTING MATERIAL

Expt. No.	Sample: Boiling range	Sample: Hydrolyzable chlorine	Sample: Classed to the Main fraction	Hydrolyzate: Weight	Hydrolyzate: Yield
	°C	%		g.	%
1	28.5–29.0	22.9	A	30	78
2	30.1	28.7	A	195	68
3	30.1–33.5	34.6	A	250	71
4	34.0–34.5	39.8	B	135	69
5	34.8–35.4	40.0	B	210	77
6	35.4–35.9	42.7	B	140	81
7	36.0–37.0	46.7	C	120	73
8	37.5–38.1	49.5	C	100	68
9*	38.8–	53.7	C	290	76
10**	26 –40	40	—	870	79

* Residue of the distillation of Expt. 1 to 8.
** Starting material.

The results obtained with the residue of redistillation and the starting material are also given in Expt. 9 and 10, respectively. By the hydrolysis, the formation of gelatinous mass was found in Expt. 3 and 4 which may be contaminated by (IV'). In Expt. 9 some gelatinous mass and viscous oil resulted.

Throughout this experiment, the distillation of the hydrolyzate was carried out through a semimicro Stedman column of about 50 theretical plates. By distillation, tetramethylsilane (I') distilled out at first, then a small amount of hydrocarbon boiling at 33°–37°C and the succeeding plateaus of $\mathbf{M}_2'$, $\mathbf{M}'\mathbf{D}'\mathbf{M}'$, $\mathbf{M}'\mathbf{D}\mathbf{M}'$, $\mathbf{D}_4'$ and $\mathbf{M}'\mathbf{D}_2'\mathbf{M}'$ were obtained at 70°, 117°, 128°, 133° and 154°C. respectively. The small plateau $\mathbf{M}'\mathbf{D}\mathbf{M}'$ appeared in the fraction A and B and its amount was found to be about 5% of $\mathbf{M}_2'$. The presence of $\mathbf{D}_4'$ was assumed by its higher refractive index at its boiling point in the hydrolyzates of the fraction C. while in Expt. 8 and 9 the small plateau of $\mathbf{D}_4'$ was found.

In calculating the percentage composition. $\mathbf{M}'\mathbf{D}\mathbf{M}'$ and $\mathbf{D}_4'$ were included into the trimer

11) Dow-corning Silicone Notes.
12) H. J. Fletcher and M. J. Hunter, *J. Am. Chem. Soc.*, **71**, 2918 (1949).

fraction and the intermittent fraction between the succeeding plateaus was assigned to both sides fractions by cutting on the distillation curve. The percentage composition of the hydrolyzate plotted against the chlorine content of the samples (Expt. 1-9) is shown in Fig. 2.

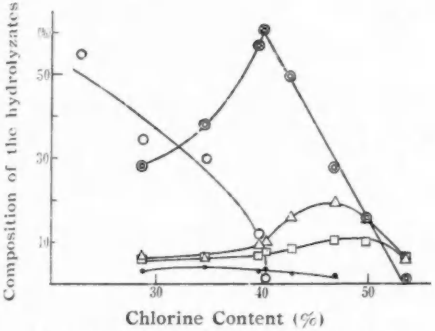

Fig. 2. Composition of the hydrolyzates with regard to the chlorine content of the redistillates.
● Hydrocarbon by-product
○ Tetramethylsilane ◎ Disiloxane
△ Trisiloxane □ Tetrasiloxane

From Fig. 2, the distribution of the components of the starting materials will be assumed.

Tetramethylsilane and Hydrocarbon By-product.—Crude tetramethylsilane (I′) was shaken with a dilute sodium hydroxide solution and redistilled. A small amount of fore-run and then the constant boiling fraction having the constant refractive index was obtained.

b.p. 26.5°–26.6°C, n_D^{10} 1.3649, d_4^{10} 0.6495.

MR_D Found: 30.34, Calcd.[10] for (I′): 30.28.

(Reported: n_D^{20} 1.3588[2], d_4^{20} 0.6399[2] and 0.646[1] b.p. 26.64°[1] and 25.5°C[2])

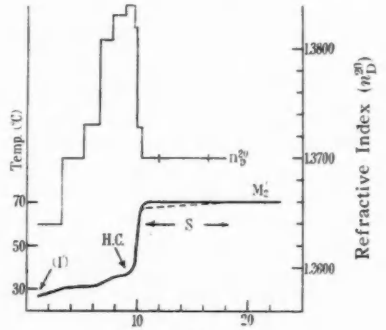

Fig. 3. An example of the redistillation curve of the hydrocarbon by-product (H. C.) and disiloxane (M_2').
Dotted line ---- shows the curve when the silanol is present.

As described above, a small plateau was found at 33°–37°C by the distillation of A and B. In some experiments, the fractionation was carefully carried out at the reflux ratio of 40–50 and the distillate was divided into many small fractions. The stepwise rise of the refractive index was observed as shown in Fig. 3.

The qualitative test, by taking a sample in a capillary and burning it slowly on a flame, gave a whit silicious smoke or white residue stuck at the end of the capillary with the samples of lower refractive index, but with the samples of higher refractive index this characteristic of the silicon compound was not found. The analysis for the fraction (n_D^{20} 1.3785) gave a high carbon content (Found: C, 80.96%; H. 14.18%).

From these data, the rigorous separation from the contaminating silicon compound, probably (I′), may be questionable and the determination by what kind of hydrocarbon the hydrolyzate is contaminated was not successful.

Isolation and Characterization of the Methylhydropolysiloxanes

Disiloxane (M_2').—As shown by the dotted line on Fig. 3, the gradually rising plateau (S) at 68°–70.5°C was obtained after the hydrocarbon by-product had distilled out. It was found usually that the refractive index of (S) decreased gradually from n_D^{20} 1.3715 to that of M_2' (n_D^{20} 1.3700). During the course of distillation in this temperature range, droplets of water were observed to accumulate gradually in the outlet tube of the column. The formation of water may be assumed to be caused by the condensation of unstable silanol to disiloxane.

$$2H(CH_3)_2SiOH \rightleftharpoons H(CH_3)_2SiOSi(CH_3)_2H + H_2O$$

By redistillation, the formation of water and the range indicated in the dotted line rapidly decreased. On repeated distillation three or four times, the formation of water has not been observed and the rigorously constant plateau of M_2' at 70.5°C, which was indicated by full line in Fig. 3, resulted.

Trisiloxanes (M′D′M′ and M′DM′).—Redistilled trisiloxanes having the constant boiling point and refractive index are given in Table II.

Tetrasiloxanes ($M'D_2'M'$, M′D′DM′ and $M'D_2M'$).—The residues of the hydrolyzates of main fractions A and B, and starting material from which $M'D_2'M'$ has been distilled out, were gathered and rigorously fractionated under reduced pressure. Between the plateaus of $M'D_2'M'$ and $M'D_3'M'$, two small plateaus appeared. The refractive index and the hydrogen evolved by aqueous sodium hydroxide were determined throughout the distillation and the results are shown in Fig. 4.

TABLE II

METHYLHYDROPOLYSILOXANES

Polysiloxane	Boiling point °C/mmHg	Refractive index n_D^{20}	Density d_4^{20}	Molecular weight Found** (Calcd.)	Molar Refraction Found (Calcd.)[10]	% H(-Si) Found***	% H(-Si) Found**** (Calcd.)
M'_2	70.5/760	1.3700	0.7545	133 (134.33)	40.26 (40.18)	—	1.45 (1.50)
M'D'M'*	117/760	1.3774	0.8245	192 (194.46)	54.37 (54.45)	—	1.54 (1.56)
$M'D'_2M'$	154/760	1.3830	0.8613	254 (254.60)	68.89 (68.72)	—	1.57 (1.58)
$M'D'_3M'$	82.5/21	1.3860	0.8897	309 (314.73)	83.06 (82.99)	1.60	1.58 (1.60)
$M'D'_4M'$	104/21	1.3882	0.9081	368 (374.86)	97.46 (97.26)	1.58	1.54 (1.61)
$M'D'_5M'$	122/21	1.3900	0.9218	425 (434.99)	111.84 (111.53)	1.61	1.51 (1.62)
M'DM'	128/760	1.3811	0.8222	208 (208.49)	58.89 (58.82)	—	0.95 (0.97)

* M' $=H(CH_3)_2SiO_{1/2}$, D' $=H(CH_3)SiO$, D $=(CH_3)_2SiO$.
** Cryoscopic measurements in benzene.
*** The sample in ethanol was reacted with aqueous sodium hydroxide.
**** The sample was reacted with butanol saturated with sodium hydroxide.

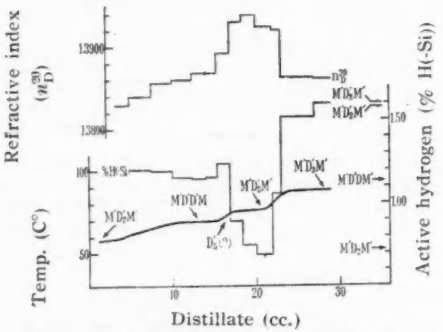

Fig. 4. Distillation curve of the intermittent fraction between $M'D'_2M'$ and $M'D'_3M'$ under reduced pressure (26 mm.).
Active hydrogen content was determined by adding aqueous sodium hydroxide to the sample in ethanol.

From the active hydrogen content, these two small plateaus were supposed to be those of M'D'DM' and $M'D_2M'$. As the amounts of these compounds were small, it may be questionable whether or not the physical constants acquired here may be taken for those of pure compounds. Further, there is a possiblity of the appearance of isomeric M'_3T in front of the plateau of M'D'DM'. This is because the branched chain polymer (M_3T: b.p. 190°C) has been reported[13] to have a slightly lower boiling point than the isomeric linear polymer (MD_2M: b.p. 194°C). Cyclopentamer D'_5 (b.p. 168.7°C, n_D^{20} 1.3912)[3] will be expected to appear between the plateaus of $M'D'_2M'$ and $M'D'_3M'$. In this experiment, no proofs were found as to its presence except the higher active hydrogen content at the back part of the plateau of M'D'DM'.

Polysiloxanes Higher than Tetrasiloxane.—Distillation was further continued and the succeeding plateaus of $M'D'_2M'$, $M'D'_3M'$, $M'D'_4M'$ and $M'D'_5M'$ were obtained at the temperature of 82.5°C/21 mm., 104°C/21 mm., 122°C/21 mm. and 87°C/2 mm. The portions having the refractive index higher than the neighbouring plateaus, a relation similar to that which is shown in Fig. 4, were found between the succeeding plateaus. The differences between the boiling points of the neighbouring plateaus became less with the distillate and it became difficult to differentiate the complete plateau from the intermittent fractions above $M'D'_5M'$. Judging from the active hydrogen content and the increment of the refrcative index of the succeeding plateaus, the plateau of 87°C/2mm. (n_D^{20} 1.3940. Found: H(-Si), 1.53%. Calcd. for $M'D'_5M'$: H(-Si), 1.63%.) was considered to be contaminated by the neighbouring compounds.

The properties of the polysiloxanes until $M'D'_5M'$ are given in Table II.

Analysis of Active Hydrogen.—The determination of % H(-Si) was carried out by using Zerewitinoff apparatus. The values in the data obtained by adding butanol saturated with sodium hydroxide to the sample or its butanolic solution, were smaler than the calculated value with $M'D'_4M'$ and $M'D'_5M'$, the causes of which may be related to the formation of gelatinous mass[14] in the reaction mixture. Accordingly, aqueous sod-

13) W.I. Patnode and D.F. Wilcock, ibid., 68, 358 (1946).

14) U. Takahashi, This Bulletin, 28, 443 (1955).

ium hydroxide was added to the sample in ethanol, as described by Sauer[3], and the satisfactory results were obtained with the higher polymers without formation of gelatinous mass. Because of the closed value of % H(-Si) as the polymer size increased, it was necessary to characterize each compound practically by means of both % H(-Si) and molecular weight.

Summary

(1) Tetramethylsilane, dimethylchlorosilane and methyldichlorosilane and a small amounts of trichlorosilane and hydrocarbon by-product were found in the lower boiling product (b. p. 26°–40°C) of silicon methylchloride reaction.

(2) Dimethylethoxysilane and methyldiethoxysilane besides small amounts of dimethyldiethoxysilane and triethoxysilane were found in the ethanolysis product.

(3) Owing to the contamination of the hydrocarbon by-product, dimethylchlorosilane could not be isolated by repeated distillation. To characterize this substance, it was synthesized from dimethylethoxysilane and benzoylchloride.

(4) By hydrolysis, linear copolymers $\mathbf{M'D'_nM'}$ and $\mathbf{M'D_nM'}$ were found. Of these, copolymers $\mathbf{M'D'_nM'}$ having two to eight silicon atoms and $\mathbf{M'DM'}$ have been characterized.

The authors wish to express their hearty thanks to the Shin-etsu Chem. Ind. Co. for giving them valuable samples.

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Some Considerations of Suspension Polymerization of Minute Droplets

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(Received September 2, 1955)

Introduction

By the study of Hohenstein and Mark[1] on suspension polymerization, it has been established that such a polymerization is equal to a summation of individual bulk processes of many droplets of monomer which are suspended in water. But more critically Haward[2] has published his study on the effect of volume change of the monomer droplet on active centre concentration, where it is assumed that the formation of an active centre is always in pairs and it is concluded that subdividion of the system, i. e., the decrease in the volume of droplets, causes the stationary value of active centre concentration to decrease.

In this discussion, we shall reconsider the subject, introducing a new quantity which represents the yield of polymer radicals from initiator fragments which are formed by the decomposition of initiator and may produce free polymer radicals.

Stationary State

We can recognize suspension polymerization processes as probability processes concerned with the appearance and disappearance of active centres, and the following probabilities are taken into consideration:

probability of appearance of one new active centre in a droplet during a time interval Δt which is very short ····· λ_1,
probability of appearance of two new active centres in a droplet during Δt ····· λ_2,
probability of disappearance of two active centres during Δt by mutual termination within a droplet which has n active centres ····· $\mu n(n-1)$, where μ is a constant,
probability that an arbitrarily chosen droplet has n active centres at time t ····· $P_n(t)$,

and (1) is given,

$$P_n(t+\Delta t)=\{1-\lambda_1\Delta t-\lambda_2\Delta t-\mu n(n-1)\Delta t\}P_n(t)+\lambda_1\Delta t P_{n-1}(t)+\lambda_2\Delta t P_{n-2}(t)+\mu(n+2)(n+1)\Delta t P_{n+2}(t)+o(\Delta t) \quad (1)$$

where $o(\Delta t)$ represents a higher order term of Δt. Formula (1) gives the differential equation (2).

$$dP_n/dt=-\{\lambda_1+\lambda_2+\mu n(n-1)\}P_n+\lambda_1 P_{n-1}+\lambda_2 P_{n-2}+\mu(n+2)(n+1)P_{n+2} \quad (2)$$

In order to solve (2), we introduce a generating function B, i. e.,

$$B=\sum_{n=0}^{\infty} P_n S^n$$

1) W.P. Hohenstein and H. Mark, *J. Polymer Sci.*, **1**, 127 (1946).
2) R.N. Haward, *J. Polymer Sci.*, **4**, 273 (1949).

and (3) is given.

$$\partial B/\partial t=\mu(1-s^2)\partial^2 B/\partial s^2 -\{(\lambda_1+\lambda_2)-\lambda_1 s-\lambda_2 s^2\}B \quad (3)$$

Using a new quantity f, which is the yield of polymer radicals from initiator fragments, λ_1 and λ_2 are represented as follows, provided that Δt is sufficiengly short,

$$\lambda_1=2\varphi Vf(1-f),\quad \lambda_2=\varphi Vf^2 \quad (4)$$

where φ is the rate of formation of initiator fragments and V is the average volume of droplets. μ is proportional to $1/V$ and represented by (6), where k_t is the chain termination reaction constant.

$$\mu=k_t/V \quad (5)$$

(3), (4) and (5) give (6).

$$\partial B/\partial t=k_t(1-s^2)\partial^2 B/\partial s^2/V -\varphi Vf(1-s)\{2-f(1-s)\}B \quad (6)$$

It is difficult to obtain the solution of (6) generally, and we shall discuss the stationary state only.

In the stationary state, $\partial B/\partial t=0$, and (7) is given,

$$(1-s^2)\partial^2 B/\partial s^2=\varphi V^2 f(1-s)\{2-f(1-s)\}B/k_t \quad (7)$$

which can be solved approximately.

Now we wish to estimate active centre concentration R. There exists a relationship (8) between R and M, where M is the average number of active centres per droplet, as represented by (9).

$$R=M/V \quad (8)$$

$$M=\sum_{n=1}^{\infty} nP_n \quad (9)$$

Using (7), (8) and (9), we can estimate the approximate numerical values of R (Appendix). Variations in f and V alter the values of R. These are shown in Table I. When

TABLE I

$f\sim V\sim R$ RELATIONSHIPS

f	V	m	P_0	P_1	P_2	M	R	$R:1.2V$
1	$\sqrt{k_t/\varphi}\times 1/3.16$	0.1	0.909	0	0.091	0.182	$V\varphi/k_t\times 0.575$	0.364
	〃 1/10	0.01	0.990	0	0.010	0.020	〃 0.200	0.040
	〃 1/31.6	0.001	0.999	0	0.001	0.002	〃 0.063	0.004
	〃 1/100	0.0001	1.000	0	0.000	0.000	〃 0.000	0.000
0.99	〃 1/3.16	0.1	0.476	0.492	0.024	0.540	〃 1.71	1.080
	〃 1/10	0.01	0.498	0.499	0.003	0.504	〃 5.04	1.008
	〃 1/31.6	0.001	0.500	0.500	0.000	0.500	〃 15.8	1.000
	〃 1/100	0.0001	0.500	0.500	0.000	0.500	〃 50.0	1.000
0.75	〃 1/3.16	0.1	0.478	0.493	0.022	0.538	〃 1.70	1.076
	〃 1/10	0.01	0.499	0.500	0.000	0.500	〃 5.00	1.000
	〃 1/31.6	0.001	0.500	0.500	0.000	0.500	〃 15.8	1.000
	〃 1/100	0.0001	0.500	0.500	0.000	0.500	〃 50.0	1.000
0.50	〃 1/3.16	0.1	0.482	0.494	0.018	0.530	〃 1.67	1.060
	〃 1/10	0.01	0.499	0.500	0.000	0.500	〃 5.00	1.000
	〃 1/31.6	0.001	0.500	0.500	0.000	0.500	〃 15.8	1.000
	〃 1/100	0.0001	0.500	0.500	0.000	0.500	〃 50.0	1.000
0.25	〃 1/3.16	0.1	0.490	0.496	0.011	0.517	〃 1.63	1.034
	〃 1/10	0.01	0.499	0.500	0.000	0.500	〃 5.00	1.000
	〃 1/31.6	0.001	0.500	0.500	0.000	0.500	〃 15.8	1.000
	〃 1/100	0.0001	0.500	0.500	0.000	0.500	〃 50.0	1.000
0.01	〃 1/3.16	0.1	0.500	0.500	0.000	0.500	〃 1.58	1.000
	〃 1/10	0.01	0.500	0.500	0.000	0.500	〃 5.00	1.000
	〃 1/31.6	0.001	0.500	0.500	0.000	0.500	〃 15.8	1.000
	〃 1/100	0.0001	0.500	0.500	0.000	0.500	〃 50.0	1.000
0	no reaction					0	〃 0	0

It is shown in this table that R, regarded as a function of f, changes discontinuously at two points, i.e., $f=0$ and $f=1$. This is a reasonable result from the difference between two boundary conditions which have been used in the course of solving (7), and completely right so far as stationary states are discussed ($t\longrightarrow\infty$). At a stationary state which has been attained after a long enough period of reaction, there exist significant differences of active centre distributions between $f=1$ and $f=0.99$ or $f=0$ and $f=0.01$.

On the other hand, it is naturally thought that at the beginning of a reaction there should be little differences of active centre distributions between $f=1$ and 0.99 or $f=0$ and 0.01. Therefore, R ought to change continuously in the whole range of $0\leqq f\leqq 1$ if t takes some finite value, sometimes taking a stationary value and sometimes an unstationary one, as f varies. Actually, such a $R\sim f$ relationship at a constant finite t is the matter to be discussed. A general discussion of this would require a general solution of (6), which will not be touched on in this paper. Only the case when V is extremely small will be discussed in the next section.

f is zero, R equals zero and polymerization does not occur. When f is unity, the decrease in V causes R to decrease. When f is between zero and unity and equals neither of them, the decrease in V increases R to a maximum, $1/2V$, which is approached more and more as V decreases. The greater values of R, in this case, mean not only higher rates of polymerization reaction, but also higher degrees of polymerization of products, since the greater values of R at the same initiation rate are caused only by longer lives of molecular chains. We can know, therefore, that the subdivision of the system makes both the rate and degree of polymerization lower when $f=1$, and higher when $0<f<1$.

Of course, the above discussion is based on the assumption of a stationary state, and the length of time it takes for R to reach the stationary value is not given here.

Initial Stages of Polymerization

The usual suspension polymerization should show a very similar figure at its initial stage to bulk polymerization, if it is true that suspension polymerization is a summation of bulk polymerizations of dispersed monomer droplets. The time necessary for R to reach half of the stationary value is $(k_t\varphi f)^{-1/2}$ which is independent of V[3], provided that V is very great as compared with $1/R_\infty$[4]*.

In the case of suspension polymerization of minute droplets, on the other hand, it has been established in this paper that the stationary value of R approximately equals $1/2V$ when $0<f<1$ is satisfied. In this case the probabilities that a droplet contains no active centre and one are both 1/2. And an active centre freshly created in a droplet which contains another active centre previously created, quickly terminates together with the old one, and the probability of coexistence of two or more growing active centres in one droplet is very small as compared with unity. In this case we can make the following approximate expression,

$$v_t=4\varphi f(1-f)VR$$

where v_t is the disappearance rate of active centre (rate of chain termination reaction), and $0<f<1$ is assumed. It gives

$$dR/dt=(\lambda_1/V)-v_t=2\varphi f(1-f)(1-2VR),$$

which being integrated, gives (10).

$$R=[1-\exp\{-4f(1-f)\varphi Vt\}]/2V \qquad (10)$$

When t goes to infinity, R goes to $1/2V=R_\infty$. The time necessary to reach the half value of R_∞, or the measure of quickness with which R approaches to stationary value, is expressed by τ in (11).

$$\tau=\ln 2/4f(1-f)\varphi V \qquad (11)$$

This relationship is shown in Fig. 1.

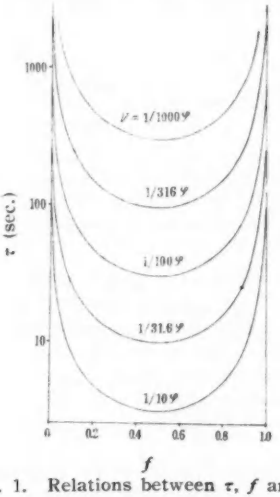

Fig. 1. Relations between τ, f and V.

If we estimate the numerical values of φ, f, and V, the numerical value of τ is known. Nozaki and Bartlett[5] have shown that the decomposition rate of benzoyl peroxide in methyl methacrylate at 60°C is 0.36×10^{-5}/sec., which means that φ is 0.72×10^{-5} (BPO) mol./l. sec. If V is smaller than $\ln 2/4f(1-f)\times0.72\times10^{-5}$ (BPO), τ is greater than one second, and the decrease in V proportionally increases τ. If V is much smaller than this, τ is much greater than unity and the decrease in V ultimately increases τ so much that the stationary state would not be reached at any late stage of reaction.

Nevertheless, R in the case of the smaller V is always greater than R in the case of the greater V at the same reaction time. This is shown in Fig. 2. The greater values of R in such cases mean not only the higher reaction rates, but also the higher degrees of polymerization of products as indicated in the previous section.

We can know, therefore, that the suspension polymerization of minute droplets should show high values in both rate and degree of polymerization than usual suspension process in either initial (unstationary) or stationary stages of reaction. In other words, a system of suspension polymerization, subdivided to smaller and smaller droplets should

3) W.H. Stockmeyer, *J. Chem. Phys.*, **12**, 143 (1944).

4) This is satisfied in the case of usual suspension polymerization. Ref. 2).

* R_∞ is the stationary value of R. See the latter part of this section.

5. K. Nozaki and P.D. Bartlett, *J. Am. Chem. Soc.*, **68**, 2377 (1946).

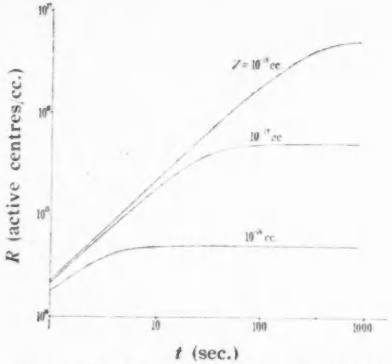

Fig. 2. $R \sim t$ relationships as for (BPO)=0.1 mol./l.

ultimately shift to a system where both rate and degree of polymerization are greater than when undivided, provided that $0<f<1$ is satisfied. This agrees with the observation by Hohenstein and Mark[1] that the rate is increased in suspension polymerization, when agitation is done vigorously.

Emulsion Polymerization Accelerated by Oil-soluble Initiator

Following the practice that the polymerization of monomer emulsion by water-soluble initiator is called emulsion polymerization, we usually name the polymerization of monomer emulsion by oil-soluble initiator also as emulsion polymerization. These two are, indeed, common in that rate accelerating and molecular weight increasing effects are observed as compared with bulk or suspension polymerization in the same condition. But the two emulsion polymerizations cannot be the very same ones because of the difference in the modes of free radical appearance into polymerization loci, viz., one by one in the former and two at once in the latter.

There coexist in monomer emulsion two sorts of monomer dispersions, i.e., emulsified droplets and solubilized monomer in soap micelles[6]. In the case of emulsion polymerization accelerated by oil-soluble initiator, polymerization should occur in both of them. A study on BPO-initiated emulsion polymerization of methyl methacrylate, worked by Kagawa and the author[7], showed, in addition to the above mentioned rate and molecular weight increasing effects, that the turbidity decreased as reaction proceeded, which suggested that the polymerization in micelle is preferential.

The preceding authors[8] imagined some mechanisms agreeable with the characteristic figures of emulsion polymerization, accelerated by oil-soluble initiator, i.e., capture of free radicals by aqueous phase, and pre-existing of free radicals in reaction system etc. But now, these are unnecessarily essential to illustrate the characteristic figures of emulsion polymerization accelerated by oil-soluble initiator. We can do it by assuming only $0<f<1$, as follows.

Solubillzed monomer in micelles are very small crowds of monomers and can be recognized as extremely small monomer droplets. If $f=1$, the value of R should be very near to zero in micelles because of their smallness and micelles should not contribute to the reaction practically. So the reaction should proceed only in the emulsion droplets. On the other hand, when $0<f<1$, R in the micelles should be very great because of their smallness and reaction in the micelles should surpass that in droplets which in this case serve almost only as reservers of monomers, and decrease in turbidity is expected. Therefore, the above-mentioned experimental results by Kagawa and Kaichi are simply illustrated by assuming $0<f<1$. This condition ($0<f<1$) is perhaps satisfied in all oil-soluble initiators because the mutual reaction between two decomposition fragments can always be considered[9].

Thus we can understand suspension polymerization and emulsion polymerization accelerated by oil-soluble initiator on a simple common basis that there is no essential difference in mechanisms and only volume difference of reaction loci between these two.

Conclusion

Systems of suspension polymerization, subdivided into smaller and smaller droplets, should shift ultimately to those where both the rate of reaction and the degree of polymerisation are greater than the initial, provided that the yield of polymer radicals from initiator fragments equals neither zero nor unity. The characteristic figure of emulsion polymerization accelerated by oil-soluble initiator can be understood on this basis.

Appendix

Estimation of R from Formulae (7), (8) and (9)

The stationary state assumption gives (i), when we represent the numbers of droplets which contain odd and even numbers of active centres by N_o and N_e, respectively,

$$dN_o/dt=\lambda_i(N_e-N_o), \quad dN_e/dt=\lambda_i(N_o-N_e) \quad \text{(i)}$$

6) W.d. Harkins, *J. Am. Chem. Soc.*, **69**, 1428 (1947).
7) S. Kaichi and I. Kagawa, *J. Chem. Soc., Japan* (Ind. Chem. Section), **58**, 509 (1955).
8) Ref. 2); Ref. 7).
9) M.S. Matheson, *J. Chem. Phys.*, **13**, 584 (1945).

which gives (ii).

$$(N_e-N_o)/(N_e+N_o)=\exp(-2\lambda_i t) \qquad \text{(ii)}$$

(A) $\lambda_i=0$

This means $f=0$, or $f=1$.

a) $f=0$ No reaction.

b) $f=1$ This means the formation of active centers exclusively in pairs.

(ii) gives (iii).

$$\left.\begin{array}{l} N_o=0 \\ \therefore \quad \sum P_{2i+1}=0 \end{array}\right\} \quad \therefore \quad B_{s=-1}=1$$
$$\left.\begin{array}{l} N_e=N_e+N_o \\ \therefore \quad \sum P_{2i}=1 \end{array}\right\}$$
$$\left.\begin{array}{l} N_e+N_o=\text{const.} \\ \therefore \quad \sum P_n=1 \qquad \therefore \quad B_{s=1}=1 \end{array}\right\} \qquad \text{(iii)}$$

Using (iii) as boundary conditions, we obtain (iv) from (7), (8) and (9), which gives the approximate numerical values of R, neglecting higher order terms of m, where m is the abbreviation of $\varphi V^2/k_t$. (iv) is applicable to small values of V.

$$\left.\begin{array}{l} P_0=1/1+m, \quad P_1=0, \\ P_2=m/1+m, \quad P_3=0, \cdots\cdots \\ R=2m/(1+m)V. \end{array}\right\} \qquad \text{(iv)}$$

(B) $\lambda_i \neq 0$

The means $0<f<1$.

(v) is given by (ii).

$$\left.\begin{array}{l} N_e=N_o \\ \therefore \quad \sum P_{2i}=\sum_{2i+1} \qquad \therefore \quad B_{s=-1}=0 \\ N_e+N_o=\text{const.} \\ \therefore \quad \sum P_n=1 \qquad \therefore \quad B_{s=1}=1 \end{array}\right\} \qquad \text{(v)}$$

Using (v) as boundary conditions, we obtain (vi) from (7), (8) and (9), neglecting higher order terms of m, which is applicable to small values of V.

$$\left.\begin{array}{l} P_0=1/2[1+mf(2-f)/2-0.032\,mf(1-f)] \\ P_1=1/2[1+mf(2-f)/6-0.010\,mf(1-f)] \\ P_2=mf(2-f)/4[1+mf(2-f)/2-0.032\,mf(1-f)] \\ R=(P_1+2P_2)/V \end{array}\right\} \qquad \text{(vi)}$$

Above P_3 are not given because of their extreme smallness. Fig. 1 is the result of the abovementioned numerical estimations of P_0, P_1, P_2 and R by inserting several values of m and f into (iv) and (vi).

The author wishes to express his sincere thanks to Prof. Ikumi Kagawa, Nagoya Univ., for introducing him to this field of work.

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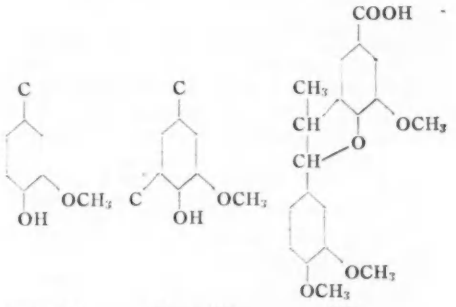
Studies on the Cooking Mechanism of Wood. XIII[1]. *On the Phenolic Hydroxyl Group of Lignosulphonic Acid*

By Hiroshi MIKAWA, Koichiro SATO, Chizuko TAKASAKI and Kiyo EBISAWA

(Received September 6, 1955)

That the lignin in situ contains phenolic hydroxyl group was definitely established by the recent investigations of Richtzenhain[2]. By methylation of wood with diazomethane followed by permanganate oxidation, he could obtain veratric acid and isohemipinic acid. This fact proves that the lignin contains two types of phenolic hydroxyl groups, (I) and (II), already in wood. As it seems to be quite improbable that some destruction of the phenolic hydroxyl group occurs during the sulphonation, the phenolic hydroxyl groups already existed in wood must exist in lignosulphonic acid too.



Type (I) Type (II) (III)

A method to estimate the amount of the phenolic hydroxyl group of the lignin in wood was worked out, and the amount was estimated

1) Part XII, This Bulletin, 28, 653 (1955); cf. also short communication, ibid., 29, 209 (1956).
2) H. Richtzenhain, *Chem. Ber.*, 83, 488 (1950).

as 0.15–0.18/CH_3O. The amount of the phenolic hydroxyl group of the solid lignosulphonic acid, i.e. sulphonated lignin contained in the wood sulphonated at neutral pH, was also measured, and it was confirmed that the content was exactly the same as that of the lignin in situ. This fact proves that no new formation of phenolic hydroxyl group occurs during the sulphonation at neutral pH.

No definite conclusion has been obtained as yet, as to whether the sulphonation reaction accompanies the formation of phenolic hydroxyl group or not. Hägglund and Carlsson observed a new formation of hydroxyl group[3], and the nature of this hydroxyl group was thought by Freudenberg to be phenolic, formed by the opening of benzopyran or fran rings[4]. Hachihama, Shinra and Kyogoku recognized a quantitative relationship between the amount of sulphur introduced and the phenolic hydroxyl group formed[5]. Freudenberg, Lautsch and Piazolo, however, could not recognize any appreciable increase of phenolic hydroxyl group by sulphonation at low temperature, although the decrease of the amount of the ether oxygen was quite appreciable[6]. One of the reasons for such discrepancies may be due to the difference of the methods used for the estimation of the phenolic hydroxyl group.

The amount of the phenolic hydroxyl group of lignin itself depends also on the methods of estimation used. By two different methods, Freudenberg estimated the amount as one/3.9CH_3O[7] and one/1.7–3.3CH_3O[8]. Aulin-Erdtman introduced a spectroscopic method, and by the method she estimated the amount of phenolic hydroxyl group of lignosulphonic acid as one/4–6CH_3O. In our present communication, her spectroscopic method was used.

Low sulphonated lignosulphonic acid, obtained from the sulphonated wood by the Kullgren process[9], has according to Aulin-Erdtman 0.13 phenolic hydroxyl group per methoxyl group[10]. Our samples showed slightly greater values, but the difference was very little. This fact proves that no new formation of phenolic hydroxyl group occurs during the Kullgren process, either. It will also be concluded, from this fact that wood seems to contain no easily hydrolizable linkages, which can produce phenolic hydroxyl group. As the lignin in wood contains two types of phenolic hydroxyl groups, (I) and (II), phenolic hydroxyl groups of low sulphonated lignosulphonic acid belong also to these two types.

According to Aulin-Erdtman[10], ordinary lignosulphonic acid contains 0.17 phenolic hydroxyl group, 0.04 more than that of low sulphonated acid. As will be stated later, a slight increase of phenolic hydroxyl group was also recognized in the acidic further sulphonation of low sulphonated lignosulphonic acid, i.e. in the sulphonation of B-group region. Freudenberg showed previously, that the so-called Erdtman's acid (III) was sulphonatable by acidic sulphite solution, accompanying the formation of phenolic hydroxyl group by opening its coumaran structure[11]. This acid contains, however, carboxyl group in the para position to its benzyl-aryl ether bond belonging to phenyl-coumaran structure, which may affect the reactivity of the aryl ether bond. As will be stated later, dihydro-dehydro-diisoeugenol (XIV) was also found to be sulphonatable by acidic sulphite solution. Lindgren and Mikawa[12] confirmed that such structure reacts with thioglycolic acid very easily, whereby the phenyl-coumaran structure is split accompanying the new formation of phenolic hydroxyl group. Lignothioglycolic acid prepared from the completely methylated wood has about 0.16–0.2 phenolic hydroxyl group per methoxyl. This fact provides a possibility that the lignin in wood contains at most about this amount of phenyl-coumaran structure with benzyl-aryl ether linkage. From these experimental findings, it will reasonably be assumed, that such phenyl-coumaran structure exists in lignin, and a part of the B group must have such structure.

As stated previously, low sulphonated lignosulphonic acid contains two types of phenolic hydroxyl group, that of type (I) and (II). The sulphonation of B group accompanies the new formation of phenolic hydroxyl group, which is expected to belong to type (II), since a part of the B group may have phenyl-coumaran structure having benzyl-aryl ether bond. It will, therefore, be very interesting to know the amount of both these phenolic hydroxyl groups belonging to different types, in various lignin preparations. Conductometric titrations of many model compounds

3) E. Hägglund and G. Carlsson, *Biochem. Z.*, 257, 467 (1933).
4) K. Freudenberg, *Annual Rev. Biochem.*, 8, 81 (1939).
5) Y. Hachihama, H. Shinra and Y. Kyogoku, *J. Soc. Chem. Ind. Japan*, 47, 212 (1944).
6) K. Freudenberg, W. Lautsch and G. Piazolo, *Cellulosechem.*, 22, 97 (1944).
7) K. Freudenberg and H. Walch, *Ber.*, 76, 305 (1943).
8) K. Freudenberg, *Das Papier*, 1, 209 (1947); K. Freudenberg and D. Rasenack, *Ber.*, 86, 755 (1953).
9) C. Kullgren, *Svensk Kem. Tid.*, 44, 15 (1932).
10) G. Aulin-Erdtman, *Svensk Papperstidn.*, 55, 745 (1952); 56, 91 (1953).
11) K. Freudenberg, M. Meister and E. Flickinger, *Ber.*, 70, 500 (1937).
12) B. Lindgren and H. Mikawa, *Acta Chem. Scand.*, 8, 954 (1954).

showed that the phenolic hydroxyl group of type (I), i.e. that of the simple guaiacol type, was without exception titratable, that of type (II), however, was found to be conductometrically untitratable, even a slight change of inclination not being observed in the titration curve. This fact provides a very sharp method to measure tne frequency of both types of phenolic hydroxyl group in lignin. Aulin-Erdtman[10] reports that the model compounds having the phenolic hydroxyl group of type (II) are not neutralized completely even at about pH 12. She supposes the existence of some amount of such phenolic hydroxyl group (termed "hindered" phenolic hydroxyl group by Coggeshall[13].) in lignosulphonic acid.

By this method, it was found that low sulphonated lignosulphonic acid contains both types in approximately equal amounts. As the phenolic hydroxyl group of this acid is the same with that of the lignin in situ, the phenolic hydroxyl group of the lignin in wood may consist of about equal amounts of both phenolic hydroxyl groups. α-Lignosulphonic acid contains type (II) much more than type (I), the ratio being 7 : 3 in this acid. As a part of the B group is expected to be phenyl-coumaran structure, it is quite understandable, that type (II) increased very much after the sulphonation of the B group. The content of the type (I) is higher in birch α-lignosulphonic acid than in spruce α-acid, the ratio of type (I) and (II) being about 1 : 1. This fact will easily be understood, as the titrations of model compounds show that the phenolic hydroxyl group belonging to syringyl nucleus is conductometrically titratable, which can not form phenyl-coumaran structure.

On the Amount of Phenolic Hydroxyl Group and Phenyl-coumaran Structure of Lignin in Wood

As stated previously, Richtzenhain proved definitely that the lignin in situ contains already phenolic hydroxyl group. The amount, however, was not known. Based on the yield of veratric and isohemipinic acid, the frequency of the phenolic hydroxyl group is calculated to be one per 15.4 methoxyl group. This value is, however, only the lower limit of the frequency of the phenolic hydroxyl group, as one can not estimate the loss of these acids during the oxidation.

During the preparation of lignothioglycolic acid, the most reactive groups, i.e. X, Z and B, combine with thioglycolic acid[14,15] very quickly under comparatively mild conditions, thus protecting the reactive groups and preventing secondary reaction. It will, therefore, reasonably be assumed, that the phenolic hydroxyl group of lignothioglycolic acid is the sum of the phenolic hydroxyl group of lignin already existing in wood, and of that formed during the reaction with thioglycolic acid. The latter hydroxyl group may at least partly be formed from the phenyl-coumaran structure. It is, therefore, expected that the frequency of the phenolic hydroxyl group of lignothioglycolic acid, prepared from completely methylated wood, gives the upper limit of the frequency of the phenyl-coumaran structure of the lignin in situ. The difference of the amount of the phenolic hydroxyl group of the lignothioglycolic acid, prepared from untreated wood, and that prepared from the

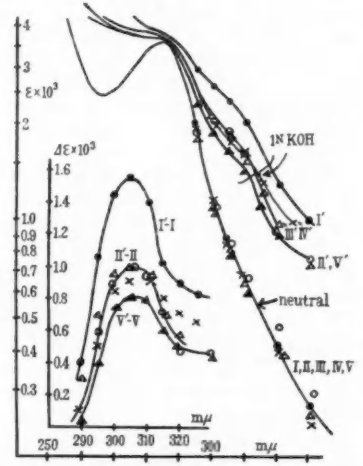


Fig. 1. UV-absorption spectra and $\Delta\varepsilon$-curves of lignothioglycolic acids prepared from various wood powders.

wood powders	CH_3O% of wood	CH_3O% of lignothioglycolic acid
(I) ● Spruce wood powder (s.)	—	11.81
(II) ○ CH_2N_2 methylated s.	11.91	13.88
(III) △ S. Sulphonated at neutral pH and then methylated with CH_2N_2	14.90	14.25
(IV) × S. methylated with Me_2SO_4	15.80	15.30
(V) ▲ 〃	22.10	16.15

13) N. Coggeshall, *J. Am. Chem. Soc.*, **69**, 1620 (1947); N. Coggeshall and A. Gtessner, ibid., **71**, 3150 (1949); **72**, 2275 (1950). cf. also Kirk-Othmer, Encyclopedia of Chem. Tech., Vol. 10, 301 (1953).

14) H. Mikawa and K. Sato, *J. Chem. Soc. Japan Ind. Chem. Sec.*, **57**, 605 (1954).

15) Part XI of this series. This Bulletin, **28**, 649 (1955).

methylated wood is expected to be the same as the amount of the phenolic hydroxyl group of the lignin in situ.

Curves (I) and (I′) of Fig. 1 are the neutral and alkaline (1 N KOH) absorption spectra of the lignothioglycolic acid prepared from untreated wood powder, (II), (IV), (V) and (II′), (IV′), (V′) are those of the lignothioglycolic acids prepared from the methylated wood powder taken in neutral and alkaline media, respectively. In (I) and (I′) the molar extinction was calculated on the methoxyl basis, the positions of the curves (II)-(V) were, however, settled by shifting them so as to give the same extinction with the Curve (I) at 282 mμ maximum. By fixing the positions of the Curves (II)-(V) in this way, the positions of the other Curves (II′)-(V′) are also fixed. Curves (I)-(V) superpose each other almost completely over the whole range of wave-lengths. So-called $\Delta\varepsilon$-curves obtained from these neutral and alkaline spectra are shown in the same figure. (I′)-(I) is the value obtained for the lignothioglycolic acid prepared from the untreated wood powder, (II′)-(II) is from the diazomethylated wood powder (CH_3O 11.9%). In order to comfirm, whether the methylation with diazomethane is complete or not, wood powders methylated with dimethyl sulphate up to CH_3O 15.80 and 22.10% were also investigated. The curve obtained for the latter is (V′)-(V). The difference of (I′)-(I)=1550 and (V′)-(V)=800, i.e. 750 corresponds to the amount of the phenolic hydroxyl group of the lignin in wood, the amount being 0.18-0.15/CH_3O by assuming the $\Delta\varepsilon$ value for monophenols as 4000-5000, according to Aulin Erdtman.

As seen in the figure, the amount of the phenolic hydroxyl group of the lignothioglycolic acid prepared from diazomethylated wood and from the wood sulphonated at neutral pH followed by diazomethylation (Curves (III) and (III′)) is approximately the same, which fact proves that no new phenolic hydroxyl group was formed during the sulphonation at neutral pH. The phenolic hydroxyl group corresponding to (V′)-(V), i.e. $\Delta\varepsilon$=800 or one per 5-6.3 CH_3O=0.16-0.2/CH_3O, is that formed during the reaction with thioglycolic acid, and this amount is expected to be the upper limit of the amount of the phenyl-coumaran structure in lignin.

On the Increase of Phenolic Hydroxyl Group of Low Sulphonated Lignosulphonic Acid by its Further Sulphonation

In a previous communication[15], further sulphonation of low sulphonated lignosulphonic acid was studied. The amount of the phenolic hydroxyl group of many sulphonic acids prepared at that time was measured by spectroscopic method, and the values thus obtained were plotted against the time of the sulphonation (Fig. 2). In this figure,

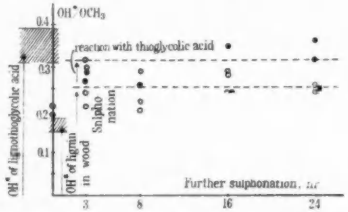


Fig. 2. Amount of the phenolic hydroxyl group of low sulphonated lignosulphonic acid (LSLSA) (○), LSA obtained by acidic further sulphonation of LSLSA (○) and of these acids after the reaction with thioglycolic acid (●). $\Delta\varepsilon$ value of monophenols was assumed to be 4000.

lignosulphonic acid corresponding to time zero is the low sulphonated lignosulphonic acid used. As stated previously, the amount of the phenolic hydroxyl group of this acid is approximately the same as that of the lignin in situ.

As can be seen in the figure, the content of the phenolic hydroxyl group increases about 0.1/CH_3O by further sulphonation. As stated previously, this newly formed phenolic hydroxyl group may be of type (II) formed by the opening of the phenyl-coumaran structure. As low sulphonated lignosulphonic acid contains phenolic hydroxyl groups belonging to type (I) and type (II) in equal ratio with the lignin in situ, the content of the type (II) must be higher in α-lignosulphonic acid. It will, therefore, be very interesting to measure the ratio quantitatively.

Conductometric Titrations of Model Compounds and the Method of the Estimation of Both Type (I) and Type (II) Phenolic Hydroxyl Group

In a previous communication[15], it was shown that the conductometrically observable so-called weakly acidic group of lignosulphonic acid consists of weak carboxyl group and the "conductometrically titratable" phenolic hydroxyl group. As an example, the curves of the conductometric titration of low sulphonated lignosulphonic acid are shown in Fig. 3. With extremely thin cell, UV-absorption spectra were taken at points A, B, C, D and E of the conductivity curve by using the

16) Part XII of this series, *loc. cit.*

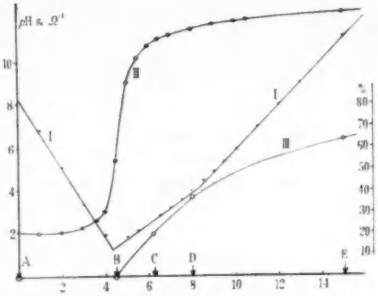


Fig. 3. Conductometric titration (I) and potentiometric titration (II) of low sulphonated lignosulphonic acid, and the percentage of the ionized phenolic hydroxyl group measured during the titration (III).

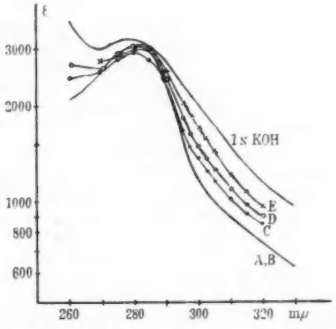


Fig. 4. UV-absorption spectra taken at points A-E of Fig. 3.

same technique as mentioned in the previous communication. (Fig. 4). The differences of the spectra taken at B-E, and in 1 N KOH, and the spectrum taken at A were indicated in Fig. 5. The percentage of the ionized

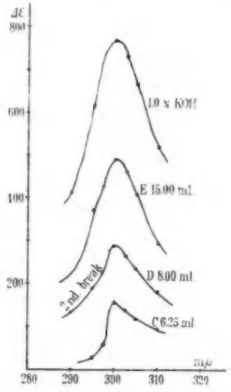


Fig. 5. $\Delta\varepsilon$-curves obtained at points C~E of the conductometric titration curve of the low sulphonated lignosulphonic acid shown in Fig. 3.

phenolic hydroxyl group at various stages of the titration calculated from Fig. 5 is shown by Curve (III) of Fig. 3. As can be seen, the phenolic hydroxyl group, which remains unionized before the second break, amounts to approximately 55% of the total phenolic hydroxyl group.

As discussed in the previous papers, simple

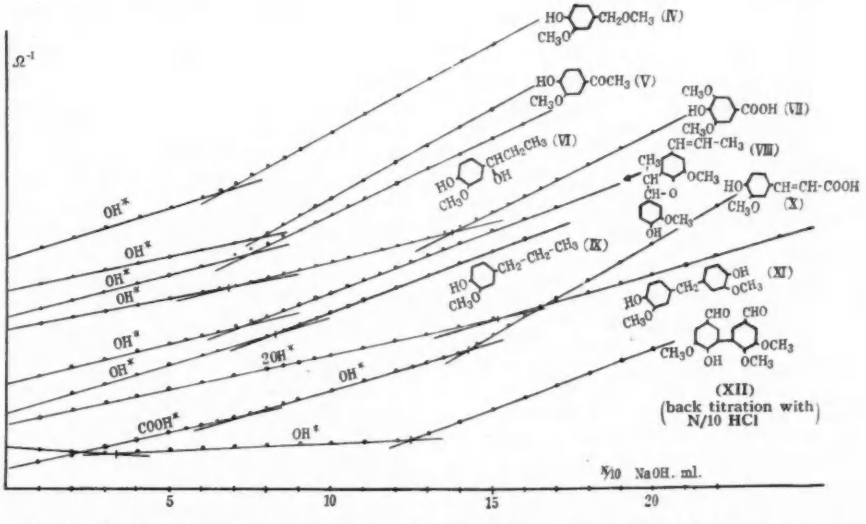


Fig. 6. Conductometric titrations of various model compounds in 30~50% aqueous alcohol. (Almost quantitative values are obtained in every case)

guaiacol type phenolic hydroxyl group was expected to be titratable. In order to confirm it, many model compounds were titrated conductometrically in aqueous alcohol (30–50%). As can be seen in Fig. 6, all these compound were titrated quantitatively without exception. As it is known that pK values of phenols are larger in alcohol than in water[17], guaiacol type phenolic hydroxyl group must be titratable in aqueous solution too, as they are titrable in aqueous alcohol. As an example of a water soluble model, vanillyl sulphonic acid was titrated in the previous communication. Another water soluble compond. guaiacyl glycerol (XVII) was titrated (Fig. 7),

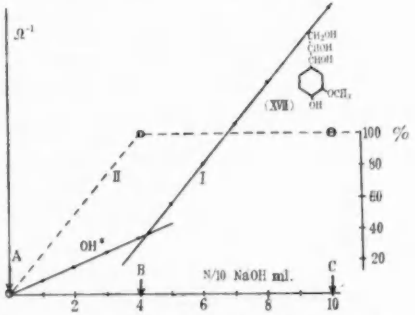


Fig. 7. Conductometric titration (I) of guaiacyl glycerol and the percentage of the ionized phenolic hydroxyl group measured at points A∼C (II).

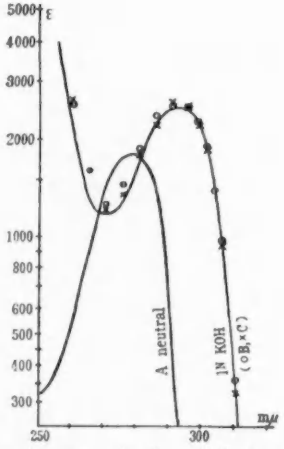
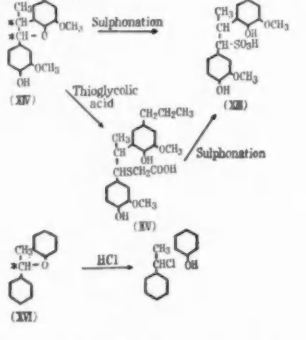


Fig. 8. Change of the UV-absorption spectrum during the titration of guaiacyl glycerol shown in Fig. 7.

As the titration proceeds along the Curve (I), the phenolic hydroxyl group ionized along the Curve II and at point B, i.e. at the end point of the titration, the ionization of the phenolic hydroxyl group was spectroscopically complete (Fig. 8). Based on these experimental findings, it will reasonably be concluded, that at the end point of the conductometric titration of the "conductometrically titratable" phenolic hydroxyl group, this group must be completely in phenolate form, i.e. that the conductometric titration and the ionization of the phenolic hydroxyl group proceeds pararell in equal amounts.

As an example of the phenol belonging to type (II), a model compound (XIII) was titrated.

This compound was synthesized by sulphonating racemic dihydro-dehydro-diisoeugenol (XIV) or its thioglycolic acid adduct (XV) with acidic sulphite solution. (XIII) was obtained in crystalline form as its benzylthiuronium salt having a sharp melting point. The structure of this compound was concluded from the analyses and its UV-absorption spectra, taken in acidic and in alkaline media shown in Fig. 10. As dihydro-dehydro-diisoeugenol contains two asymmetric carbon atoms, the product is expected to be a mixture of two different racemic modifications, provided that the racemization at the α-carbon atom is involved in the reaction. As the product was obtained, however, in crystalline form, having a sharp melting point, it appears that the compound isolated may be one of the two expected racemic modifications, if the reaction involves racemization at the α-carbon atom. It may, however, also be possible that the reaction proceeds under complete retention or complete inversion of the benzylaryl ether bond resulting in a formation of only one racemic modification. In connection with this problem, it may be remarked that Hart[18] reports that the configuration of α-phenoxy ethylbenzene (XVI) is not altered when its benzylaryl ether bond is split by hydrogen chloride.



As can be seen from the Curve (I) of Fig. 9, the amount of the conductometrically titratable

17) W. Treadwell and G. Schwarzenbach, *Helv. Chim. Acta*, **11**, 386 (1928).

18) H. Hart and H. Eleuterio, *J. Am. Chem. Soc.*, **76**, 1379 (1954).

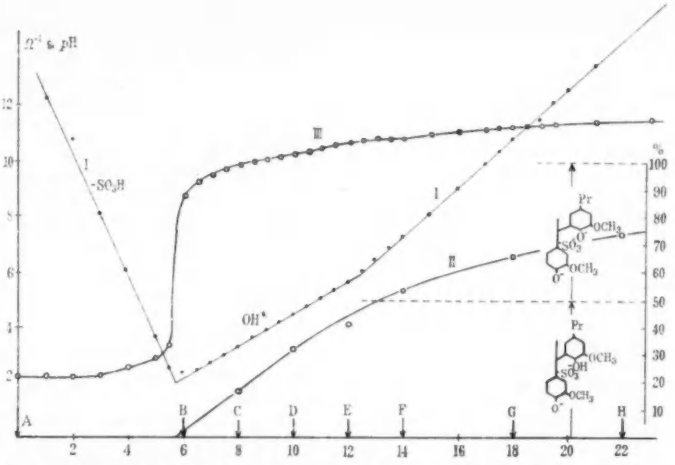


Fig. 9. Conductometric (I) and potentiometric (III) titrations of the model compound (XIII) and the percentage of the phenolic hydroxyl group ionized during the titration.

phenolic hydroxyl group is equivalent to the amount of the sulphonic acid group, i.e. only one phenolic hydroxyl group is conductometrically titrable, which is expected to be a simple guaiacol type. Curve (II), which indicates the ionization of the phenolic hydroxyl group during the titration, shows that only 50% of the total phenolic hydroxyl group is ionized at the second break of the titration curve. Even after the second break, the ionization of the remaining phenolic hydroxyl group proceeds only gradually; no quantitative relation exists, however, between the added alkali and the increase of the ionization, the phenolic hydroxyl group titrated in this region being too weak and the hydrolysis of the phenolate ion being consequently too great. Even a slight change of inclination was not observed in the titration Curve (I) around the expected third break, 18 ml. region. UV-absorption curves measured at A-H and the corresponding $\Delta\varepsilon$ curves are shown in Fig. 10 and 11 respectively.

From these experimental findings, it will be possible to conclude as follows. Potentiometric titration cannot differentiate the phenolic hydroxyl group of type (I) and (II). The curve of the spectroscopically determined percentage of the ionized phenolic hydroxyl group against the volume of the alkali added, i.e. for example Curve (II) of Fig. 9, does not show any distinct break between the two types of the phenolic hydroxyl groups. Although type (I) is conductometrically titratable and type (II) untitratable, it is impossible to determine the amount of both types by conductometric titration alone, as the phenolic

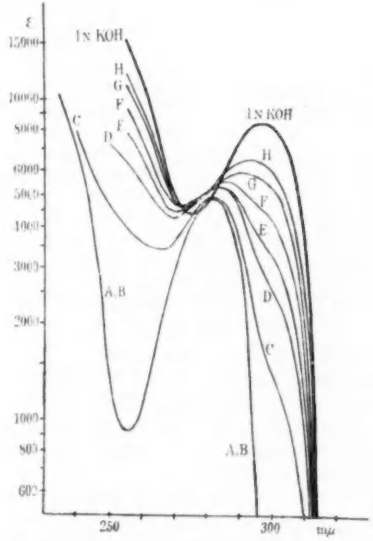


Fig. 10. Change of the UV-absorption spectrum observed during the titration of the compound (XIII) shown in Fig .9.

hydroxyl group of type (I) can not be distinguished by conductometric titration from the weak carboxyl group present in lignosulphonic acid. By combining conductometric titration (Curve I) and the curve of the percentage of the ionized phenolic hydroxyl group (Curve II), one can determine very clearly the amount of both types separately, the amount of the phenolic hydroxyl group ionized before the second break being equal

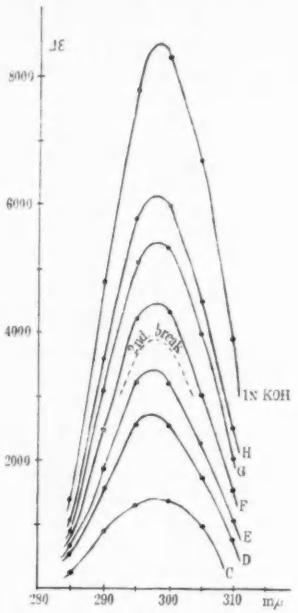


Fig. 11. $\Delta\varepsilon$-curves obtained at points C~H of the conductometric titration curve of the compound (XIII) shown in Fig. 9 and 10.

to that of type (I) and the remaining one being that of type (II).

Ratio of the Phenolic Hydroxyl Group belonging to Type (I) and Type (II) in various Lignosulphonic Acid Preparations

Fig. 3 shows the conductometric titration of the low sulphonated lignosulphonic acid and, as stated previously, about 40–50% of the total phenolic hydroxyl group was found to be conductometrically titratable and 60–50% remained untitrated in this case. The former may be of type (I) and the latter type (II). As the phenolic hydroxyl group of the lignin in wood may be the same as that of the low sulphonated lignosulphonic acid, it appears that the ratio of the phenolic hydroxyl group of the lignin in wood belonging to type (I) and (II) may be the same as that of the low sulphonated lignosulphonic acid, i.e. the amounts of these two types are thought to be about the same in this case, too.

Titration curves of an α-lignosulphonic acid was shown by Fig. 3 of the previous communication (Part XII). Only about 30% of the total phenolic hydroxyl group was conductometrically titratable. The amount of the phenolic hydroxyl group of type (II) must be, therefore, much higher in this acid than in low sulphonated lignosulphonic acid or the lignin in situ. As stated previously, the increase of the amount of type (II) may be attributed to the sulphonation of phenyl-coumaran structure in the sulphonation of B-group region.

Conductometric titration and the change of the UV-spectrum of the birch α-lignosulphonic acid are shown in Fig. 12 and 13.

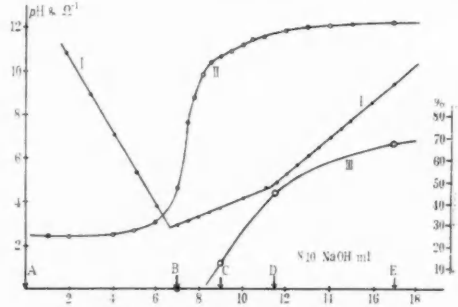


Fig. 12. Conductometric (I) and potentiometric titrations (II) of birch α-lignosulphonic acid, and the percentage of the phenolic hydroxyl group ionized during the titration (III).

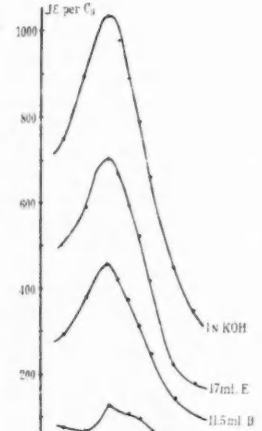


Fig. 13. $\Delta\varepsilon$-curves at points C~E of the titration curve of birch α-lignosulphonic acid shown in Fig. 12.

Conductometrically titratable phenolic hydroxyl group is about 50% of the total group in this case. The comparatively higher content of type (I) in this acid may be attributed to the existence of syringyl nucleus, which cannot form phenyl-coumaran structure. That the phenolic hydroxyl group belonging to syringyl

nucleus is conductometrically titratable was confirmed by the titration of syringic acid shown in Fig. 6.

Experimental

Methylation of various Wood Powders.—Methylation of wood powder with dimethyl sulphate was performed as usual with concentrated alkali at room temperature. Methylation with diazomethane was performed by simply keeping wood powder in etherial diazometane solution for about a week, changing the solution several times with a fresh one. Sulphonated wood powder was prepared by sulphonating at pH 6 for ten hours at 135°. Analyses of the methylated wood powders are shown in Fig. 1.

Preparation of Lignothioglycolic Acid from These Methylated Wood Powders.—To the methylated wood powder (5 g.) were added fresh distilled thioglycolic acid (25 g.) and 2N HCl (2.5 ml.), and the mixture was heated at 100° for two hours. A large amount of water was added, and the precipitate separated and washed with water by centrifuge. The residue was kept in 0.5N NaOH (50 ml.) over-night, the carbohydrate which remained insoluble was separated, and the lignothioglycolic acid was precipitated by dilute hydrochloric acid and centrifuged, washed with water, dissolved in a little amount of acetone, centrifuged and a mixture of alcohol and ether was added to the clear acetone solution of the lignothioglycolic acid. The reprecipitated lignin was washed with alcohol-ether, ether and petroleum ether successively. The yield of the cream colored powder thus obtained was 0.5–0.7 g. in every case. Analytical values are shown in Fig. 1.

Measurement of the UV-Absorption Spectra of Various Lignothioglycolic Acids.—Lignothioglycolic acid (ca. 10 mg.) was dissolved in dioxane (0.5 ml.) containing several drops of water. The solution was made up to 30 ml. with absolute alcohol purified with NaOH and zinc dust. When the spectrum in neutral medium is to be measured, 4 ml. of this solution was diluted with the same purified alcohol to 30 ml., and the alkaline spectrum was measured with the solution made by diluting 4 ml. of the solution with 60% aqueous alcohol and 3 ml. of 10N KOH, to 30 ml. The results were shown in Fig. 1.

Conductometric Titrations of Lignosulphonic Acids.—The method was the same as in the preceding papers, Part (XI) and (XII). 500 mg. of barium lignosulphonate was dissolved in 20 ml. of water, passed through cation exchanger IR 120 and the eluate was made up to 50 ml. The solution was titrated conductometrically with 0.1N sodium hydroxide solution.

Syntheses of Known Model Compounds.—Vanillyl methyl ether (IV): B. Leopold, *Svensk Papperstid.*, **55**, 816 (1952); acetovanillone (V): K. Nakazawa, *J. Pharm. Soc. Japan*, **74**, 836 (1954); α-guaiacyl propanol (VI): $LiAlH_4$ reduction of propioguaiacone acetate synthesized according to Nakazawa, loc. cit.; syringic acid (VII): M. Bogert and B. Coyen, *J. Am. Chem. Soc.*, **51** 569 (1929); Dehydro-diisoeugenol (VIII): B. Leopold, *Acta Chem. Scand.*, **4** 1523 (1950); coerulignol (IX): hydrogenation of isoeugenol with Pd-C; ferulic acid (X); Adams, Organic Reactions Vol. I, p. 250; 3, 3'-dimethoxy-4, 4'-dihydroxy-diphenyl methane (XI): H. Mikawa, *Bull. Chem. Soc. Japan*, **27**, 53 (1954); guaiacyl glycerol (XVII): E. Adler and S. Yllner, *Acta Chem. Scand.*, **7**, 570 (1953).

Synthesis of Dehydro-divanillin Monomethyl Ether (XII).—Dehydro-divanillin[19] (25 g.) was dissolved in a sodium hydroxide solution, dimethyl sulphate (30 g.) added and the methylation was performed at room temperature. Dimethyl ether separated was filtered and the filtrate was acidified with carbon dioxide. A mixture of monomethyl ether and the starting material was washed with methanol and extracted with hot benzene. The monomethyl ether thus extracted was recrystallized from benzene, m.p. 196.5–197°, yield 4.5 g.

Anal. Found: C, 64.44; H, 5.30; CH_3O, 29.5. Calcd. for $C_{17}H_{18}O_8$: C, 64.55; H, 5.10; CH_3O, 29.4%.

Synthesis and Conductometric Titration of α-(3-Methoxy-4-hydroxyphenyl)-β-(2-hydroxy-3-methoxy-5-propylphenyl)-*n*-propane Sulphonic Acid (XIII).—*Method I:* Dehydro-diisoeugenol (racemate) was hydrogenated with Pd-C to dihydrodehydro-diisoeugenol. To 4.7 g. of Di-De-Di was added 50 ml. of cooking acid (17 g. of NaOH and 50 g. of SO_2 in one liter of 50% alcohol) and the mixture was heated in a quickly rotating autoklave at 140° for twenty hours. A slight excess of sulphuric acid was added, SO_2 expelled in vacuo, and the solution was neutralized with $BaCO_3$, centrifuged, and concentrated to about 30 ml. Benzylthiuronium salt of the sulphonic acid was precipitated by adding conc. solution of benzylthiuronium hydrochloride, washed well with water, dissolved in a small amount of alcohol, filtered and reprecipitated with water. The precipitate separated at first as oil, solidified over-night. This was purified in the same way until constant m.p. was reached. M.p. 136–138°, 0.8 g. After being kept at 80° in vacuo with P_2O_5 for two days the m.p. was 145–147°.

Anal. Found: C, 58.43; H, 6.17; N, 4.98; CH_3O, 11.6. Calcd. for $C_{28}H_{31}O_7N_2S_2$ (benzylthiuronium salt of XIII): C, 58.3; H, 6.24; N, 4.86; CH_3O, 10.75%.

99.6% of the sulphonic acid group of this compound was titrated conductometrically.

Method II: 4 g. of Di-De-Di was reacted with thioglycolic acid[12] and the product XV was treated as in method I. Treating the product in the same way as above, 0.5 g. of the benzylthiuronium salt melting at 145–147° was obtained. Mixed with the product obtained by Method I, no melting point depression was observed. 0.8 g. of dihydrodehydro-diisoeugenol was recovered, which fact shows that a part of the thioglycolic acid adduct splits off its thioglycolic acid residue, regenerating the phenyl-coumaran ring.

Conductometric titration of (XIII): 400 mg. of the benzylthiuronium salt was dissolved in 10 ml. of alcohol, 20 ml. of water added and warmed. The warm solution was passed through a column

19) K. Elbs and H. Lerch, *J. prak. Chem.*, **93**, 1 (1916).

of ion exchange resin IR 120, washed with warm aqueous alcohol until neutral pH. Alcohol was boiled off in vacuo and the solution was diluted with water to 50 ml. and conductometrically titrated.

Summary

The amount of the phenolic hydroxyl group of the lignin in situ was estimated to be about one per 5-6 methoxyl. Phenolic hydroxyl group of low sulphonated lignosulphonic acid is the same as that of the lignin in situ. There exist two types of phenolic hydroxyl groups (I) and (II) in lignin and lignosulphonic acid, the former being conductometrically titratable and the latter untitratable. With several lignosulphonic acid preparations, the ratios of these two types of phenolic hydroxyl groups were measured, the ratio being 1 : 1 with lignin in wood, low sulphonated lignosulphonic acid, and birch α-lignosulphonic acid and about 3 : 7 with α-acid of gymnosperm origin. The structures of these two types of phenolic hydroxyl groups were suggested.

The anthors are indebted to Dr. H. Okada, the head of the laboratory, and to Miss. S. Suehiro for ther encouragement. They wish to express their appreciation also to Prof. Y. Hachihama Assist. Prof. Y. Kyogoku for helpful advice and during the course of the investigation.

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Studies on the Cooking Mechanism of Wood. XIV.[1] *On the UV-Absorption Spectrum, Phenolic Hydroxyl Group and Carboxyl Group of Thiolignin*

By Hiroshi MIKAWA, Koichiro SATO, Chizuko TAKASAKI and Kiyo EBISAWA

(Received September 22, 1955)

UV-Absorption Spectrum

UV-absorption spectrum of lignosulphonic acid is not so different from that of the lignin in wood[2], the minimum at about 260 mμ being rather deep and the maximum at 280 mμ comparatively sharp. This fact suggests that the structure of the building unit of lignosulphonic acid is at least optically almost uniform. UV-absorption spectrum of thiolignin has been investigated by Enkvist in order to estimate the amount of the phenolic hydroxyl group[3]. The spectra were very different from that of lignosulphonic acid and were very diffuse.

Curve (I) of Fig. 1 is the absorption spectrum of thiolignin, prepared by an experimental cook under the condition similar to that of the industrial cooking. The spectrum is very diffuse, indicating that the structure of the building units is not very uniform. The absorption around 280 mμ, calculated on methoxyl basis, is high in comparison with that of lignin or lignosulphonic acid. As the methoxyl content of thiolignin is in general not so low, except those prepared under very drastic condition or the fraction suffered an intense disintegration, the comparatively high absorbancy at this wave-length region must not be due to demethoxylation.

As will be reported later[4], benzyl alcoholic group, i. e. X group and Z group of lignin, must be exposed to high temperature alkali during the kraft cooking. Model experiments done by Leopold[5] in connection with nitrobenzene oxidation of lignin show that models with benzyl alcoholic groups (I) and (II) were split by hot alkali, resulting in a formation of carboxyl group and double bond conjugated to benzene nucleus.

Merewether recognized the existence of some amount of carbonyl group in Eucalyptus regnans thiolignin[6]. As will be reported

1) Part XIII, This Bulletin, **29**, 245 (1956).
2) P. Lange, *Svensk Papperstidn.*, **47**, 262 (1944); **48**, 241 (1945); **50**, No. 11 B, 130 (1947); G. Aulin-Erdtman, *Tappi.*, **32**, 160 (1949).
3) T. Enkvist and B. Alfredsson, *Svensk Papperstidn.*, **54**, 185 (1951).
4) Part XVI, to be published in this Bulletin.
5) B. Leopold, *Acta Chem. Scand.*, **4**, 1523 (1950).
6) J. Merewether, *Aust. J. Sci. Res., Ser.* A, **1**, 241 (1948).

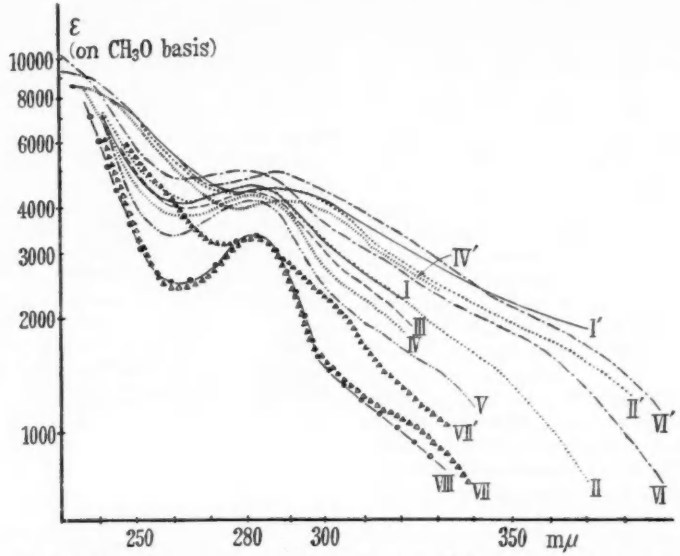
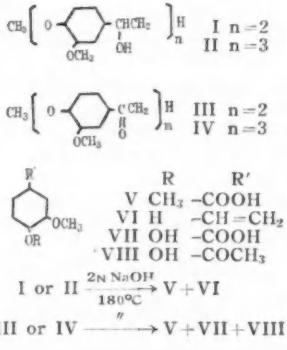


Fig. 1. UV-absorption spectrum of thiolignin, thiolignin treated in various ways, native lignin and dioxane lignin in neutral medium and in 1 N KOH.

neutral	1 N KOH	curves	lignin
I alcohol	I′ 80% alcohol	———	thiolignin
II water	II′ water	. . . . .	after sulfonation
III alcohol		— — — — —	after reduction with $NaBH_4$
IV 〃	IV′ 80% alcohol	.....	after reduction with Raney alloy
V 〃		—·—·—·—	IV after reduction with Pd-H_2
VI 〃	VI′ 〃	—·—·—·—	thiolignin prepd. from dioxane lignin
VII 〃	VII′ 〃	△△△△△△	dioxane lignin
VIII 〃		—○—○—○—	native lignin

later[4], the carbonyl group contained in thiolignin is expected, at least partly, to be conjugated with benzene nucleus, being formed at the same position, where the sulphur atom is situated, after it was split off by alkali. It is reported also that acetovanillone with such a carbonyl group is obtained from the kraft waste liquor but not from that of the soda cooking[7].

Experiments done by Leopold[5] include also reactions between high temperature alkali and model compounds with such conjugated carbonyl as those of group (III) and (IV). Formation of the carboxyl group directly connected with of benzene nucleus was observed. Not much attention has been paid to the existence of carboxyl group in thiolignin. Merewether showed, however, the existence



of carboxyl groups in a fraction containing no sulphur, separated from Eucalyptus regnans thiolignin by solvent fractionation[8].

7) T. Enkvist, M. Moilanen and B. Alfredsson, *Svensk Papperstidn.*, **52**, 53 (1949); D. Brink, R. Hossfeld and W. Standstrom, *J. Am. Chem. Soc.*, **71**, 2275 (1949).

8) J. Merewether, *Aust. J. Sci. Res., Ser. A*, **2**, 117 (1949).

Based on the model experiments discussed above and on the mechanism of the kraft cooking which will be reported later[4], the existence of the carbonyl group and the double bond conjugated with benzene nucleus and the carboxyl group directly connected to the nucleus seems to be quite probable, and it is conceived that such structures in the side chain influence the absorption spectrum of thiolignin, making it diffuse and the absorption deep. It appears, therefore, to be very interesting to investigate the influence of such treatment on the absorption spectrum of thiolignin, that the carbonyl group or double bond is expected to be eliminated.

Curve (II) is the absorption of thiolignin prepared by sulphonating (I) according to the Enkvist's method[9]. No appreciable change of the absorption was observed. (III) is the absorption of (I), measured after the reduction with sodium boronhydride, a reduction which is reported to be sufficient to reduce the carbonyl group to the hydroxyl group. The change of the absorption was not very appreciable. (IV) is the absorption of the lignin prepared from (I) by reducing it with Raney alloy and alkali. This reduction is reported to be sufficient to reduce the carbonyl group conjugated with benzene nucleus to methylene[10].

As seen in the figure, this reduction lowers the absorption at about 300 mμ very much, probably because of the complete elimination of the carbonyl group. As this lignin is expected to be completely desulphurized, one can reduce this lignin with palladium black, a catalyst which is very sensitive to sulphur. (V) represents the spectrum of thiolignin (I) reduced with Raney alloy and palladium successively. Here, the spectrum is very similar to that of native or dioxane (curves (VII) and (VIII)) lignin, all of the sulphur atom, carbonyl group and double bond in the thiolignin being eliminated by these treatments. Native lignin was isolated according to Brauns[11] and dioxane lignin according to Freudenberg[12].

These experimental results suggest to us that the absorption spectrum of thiolignin is diffuse and the absorption is higher in thiolignin than that of lignin in situ due to the presence of the carbonyl group and the double bond conjugated with benzene nucleus in thiolignin. Absorbancy shown by curve (V) around 280 mμ region is as yet higher than that of native lignin, probably because carboxyl group exists in lignin (V) as yet. As shown in Fig. 2, vanillic acid has very large absorption around 260–290 mμ region.

As stated previously, thiolignin (I) was prepared from wood powder and the thiolignin investigated by Enkvist was also prepared from wood. Absorption spectrum of thiolignin prepared from lignin without the existence of carbohydrate is not reported as yet. It is known that especially hemicellulose suffers a severe degradation during the alkaline cooking of wood. As such compounds, Sohn isolated reductic acid (V)[13] and Enkvist identified methylcyclopentenolone VI[14].

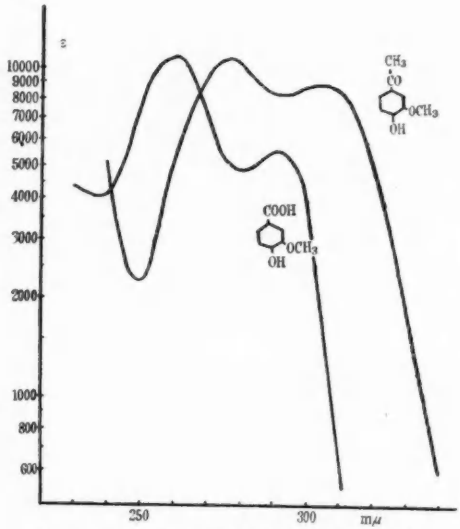


Fig. 2. UV-Absorption spectrum of vanillic acid and acetovanillone (in alcohol).

Migita and Kanda report that the color of kraft pulp is due not only to lignin but also to substances originating from hemicellulose[15]. Richtzehain assumed the condensation of lignin with some substances originating from carbohydrate during the kraft cooking in order to explain his results, that thiolignin gives a comparatively high yield of isohemipinic acid, when it is methylated with dimethyl sulphate and oxidized with permanganate[16]. It will, therefore, be con-

9) T. Enkvist, B. Alfredsson and E. Hägglund, *Svensk Papperstidn.*, **55**, 588 (1952).
10) D. Papa, E. Schwenk and B. Whitman, *J. Org. Chem.*, **7**, 587 (1942).
11) F. Brauns, *J. Am. Chem. Soc.*, **61**, 2120 (1939).
12) W. Stumpf and K. Freudenberg, *Angew. Chem.*, **62**, 537 (1951).
13) A. Sohn, *Das Papier*, **4**, 379 (1950).
14) T. Enkvist, B. Alfredsson, M. Merikallio, P. Paakbonen and O. Jarvela, *Acta Chem. Scand.*, **8**, 51 (1954).
15) N. Migita, T. Kanda, S. Mochizuki and H. Nishimura, *Japanese Tappi.*, **8**, 277 (1954).
16) H. Richtzenhain, *Svensk Papperstidn.*, **53**, 644 (1950).

ceivable that the absorption spectrum of thiolignin differs from that of the lignin in situ, because of the condensation of the substances originating from wood carbohydrate with lignin. Thiolignin was prepared, therefore, from Freudenberg's dioxane lignin under the ordinary kraft cooking condition and its spectrum was measured. The spectrum (VI) represents, however, a typical thiolignin spectrum, thus indicating that the influence of wood carbohydrate on thiolignin spectrum may not be very large and the spectrum of thiolignin must be explained by the structure of the thiolignin itself alone.

Summarizing the results, it was shown that the UV-absorption spectrum of thiolignin must be explained by assuming the existence of the carbonyl group, the double bond conjugated with the nucleus and the carboxyl group attached directly to the nucleus in thiolignin.

Estimation of the Amount of the Phenolic Hydroxyl Group and the Carboxyl Group of Thiolignin

Enkvist measured the amount of the phenolic hydroxyl group of thiolignin spectroscopically[17]. His method was, however, the old method of Aulin-Erdtman, which is not sensitive enough even when applied to simple model compounds[18].

Absorption spectra of thiolignin (I), shown in Fig. 1, which were taken in neutral and alkaline media, indicate that this lignin contains only 0.22–0.18 phenolic hydroxyl group per methoxyl group when calculated by the Aulin-Erdtman's new method[19].

The content of the phenolic hydroxyl group of thiolignin has been estimated by several different methods, and the values obtained are much greater. Enkvist titrated with sodium ethylate in ethylenediamine solution or with hydrochloric acid after addition of barium chloride to the sodium hydroxide solution of the lignin[20]. According to these methods, equivalent weight was about 200–300. Methylation with diazomethane is also used. Values measured by this method, hitherto reported, are shown in the table. The amount 0.55–0.9 per methoxyl group, being about the same as those obtained by titration methods.

As stated previously, the UV-absorption spectrum of thiolignin is rather complex,

	MeO %	After CH_2N_2 methylation MeO %	After CH_2N_2 methylation followed by hydrolysis MeO %	COOH+OH* per MeO	OH* per MeO	OH* per MeO spectroscopically measured	Literature
Alkali lignin A (spruce)	14.9	22.2		0.55			21)
Alkali lignin B (spruce)	14.0	24.8		0.87			21)
Thiolignin (spruce)	14.6	24.8		0.79			22)
Thiolignin (spruce)	12.9	23.1		0.89			3)
Alkali lignin (oat straw)	14.8 14.7	23.5 22.4					23)
Thiolignin (Eucalyptus)	21.1	27.1					24)
Native lignin (spruce)	14.8	21.4		0.49		0.4 −0.32	25)
Dixane lignin (Picea jezoensis)	15.56	17.98	17.23	0.16	0.12	0.2 −0.16	
Thiolignin I (Picea jezoensis)	15.31	23.3	20.81	0.58	0.40	0.225 −0.18	
Thiolignin prepd. from dioxane lignin	14.55						

17) T. Enkvist, B. Alfredsson, *Svensk Papperstidn.*, **54**, 185 (1951).
18) G. Aulin-Erdtman, *Tappi.*, 32, 160 (1949).
19) G. Aulin-Erdtman, *Svensk Papperstidn.*, **55**, 745 (1952).
20) T. Enkvist, *Svensk Papperstidn.*, **51**, 225 (1948).
21) H. Marshall, F. Brauns and H. Hibbert, *Can. J. Res.*, **13B**, 103 (1935).
22) C. Ahlm, *Paper Trade J.*, **113**, No. 13, 115 (1941).
23) M. Phillips and M. Goss, *J. Biol. Chem.*, **114**, 557 (1936).
24) F. Lahey and J. Merewether, *Austr. J. Sci. Res.*, **A 1**, 112 (1948).
25) F. Brauns, *J. Am. Chem. Soc.*, **61**, 2120 (1939).

and the building unit seems to be not very uniform. It is, therefore, as yet open to question, whether it is justifiable or not to estimate spectroscopically the amount of the phenolic hydroxyl group of such ununiform substance as thiolignin. Diazomethylation method seems to be much more reliable in such cases.

Since thiolignin is expected to contain some amount of carboxyl group as mentioned before, one can not expect, to obtain exact values simply from the increase of the methoxyl group by diazometylation. The content of the phenolic hydroxyl group must be calculated from the difference between the methoxyl group content of the thiolignin, methylated with diazomethane followed by alkaline hydrolysis, and that of the original untreated thiolignin, the difference of the content of the methoxyl group before and after the hydrolysis being expected to show the amount of the carboxyl group in the thiolignin. The content of the phenolic hydroxyl group of thiolignin (I) estimated according to this method is 0.4 per methoxyl group, and the amount of the carboxyl group is 0.18 per methoxyl group.

As reported previously, lignin in wood contains only about 0.14 phenolic hydroxyl group per methoxyl group; the phenolic hydroxyl group increases, therefore, very much during the kraft cooking. Because of the presence of this phenolic hydroxyl group and the carboxyl group, thiolignin is very easily soluble in alkali.

Added in proof. According to the recent investigation by J. Lindberg and T. Enkvist (*Suomen Kemistilehti*, **B 28**, 23 (1955)) the spectroscopic method of the detection of the phenolic groups due to G. Aulin-Erdtman could not be used in the case of orthovanillic acid, salicylic acid, 5-carboxyvanillin and 5-carboxyvanillic acid. As it might not be improbable that thiolignin contains some amount of pherolic hydroxyl groups with a carboxyl group in its ortho position, their findings might provide us one of the reasons why herspectroscopic method of the estimation of phenolic hydroxyl groups in lignin was not suitable in the case of thiolignin preparations.

Experimental

Preparation of Thiolignin I.—Extractives free Picea jezoensis wood powder (550 g.) was cooked with 3.5 l. of white liquor of 20% sulphidity with 4% active alkali. Temperature was raised to 165° within two hours and kept at this temperature for one hour. The black liquor was acidified, filtered and the crude thiolignin obtained was dissolved in a mixture of acetone (200 ml.) and alcohol (40 ml.) and precipitated with ether. After repeated reprecipitation, the yield was 38 g.

Anal. C, 61.33; H, 5.64; S, 2.42; CH_3O, 15.31%.

Sulphonation of Thiolignin I at Neutral pH.—To 3 g. of thiolignin I was added sulphite cooking acid of pH 8 (80 ml.) and the whole was heated at 105° for two hours in a quickly rotating autoklave. Thiolignin went into solution almost completely. Sulphonic acid was separated as Ba salt as usual and analyzed. CH_3O, 14.05; SO_3H/CH_3O, 0.119.

Reduction of Thiolignin I with Sodium Borohydride.—Five grams of thiolignin was dissolved in 100 ml. of phosphate buffer, which can dissolve lignin but has as low pH as possible. 1.5 g. of $NaBH_4$ was added and kept at room temperature over-night. CH_3O, 15.08%.

Reduction of Thiolignin with Raney Alloy and Alkali.—Three grams of thiolignin was dissolved in 20 ml. of 10% alkali and was reduced with 12 g. of fine Raney alloy powder at 80–90°. CH_3O, 15.10%.

Reduction with Palladium and Hydrogen.—0.1 g. of palladium chloride was dissolved in 20 ml. of water slightly acidified with hydrochloric acid, 500 mg. of thiolignin reduced with Raney nickel added, and the lignin was dispersed by agitation. Palladium was reduced with hydrogen and precipitated on lignin, which was separated and washed by centrifuge. The precipitate thus obtained was hydrogenated in 100 ml. of alcohol for two hours at room temperature.

Hydrolysis of the Thiolignin methylated with Diazomethane.—The lignin wasl gently refluxed with 1 N alcoholic KOH for two hours.

Kraft Cooking of Dioxane Lignin.—Three hundred milligrams of dioxane lignin was dissolved in white liquor of 20% sulphidity with 4% active alkali (5 ml.) and was heated as in the case of wood powder. CH_3O, 14.55%.

Summary

It was shown that the UV-absorption spectrum of thiolignin must be explained by assuming the existence of the carbonyl group, the double bond conjugated with the nucleus and the carboxyl group attached directly to the nucleus. The amount of the phenolic hydroxyl group and the carboxyl group of thiolignin were estimated by methylating with diazomethane and subsequently hydrolyzing the methylated lignin with alkali.

The avthors wish to express their gratitude to Dr. H. Okada, the head of the laboratory, and to Miss. S. Suehiro for their encouragement.

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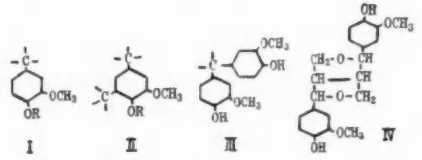
Studies on the Cooking Mechanism of Wood. XV[1]. *Mannich Reaction on Lignin Model Compounds and the Estimation of the Amount of the Simple Guaiacyl Nucleus in Thiolignin*

By Hiroshi MIKAWA, Koichiro SATO, Chizuko TAKASAKI and Kiyo EBISAWA

(Received September 29, 1955)

Introduction

Our knowledge on the side chain and nuclear structure of thiolignin is very unsatisfactory. The elucidation of this problem is of fundamental importance to find out a valuable utilization of thiolignin, which is now burned in order to recover sodium. According to the investigation of Richtzenhain[2], the yield of isohemipinic acid by permanganate oxidation of the methylated lignin preparations is higher in the case of thiolignin, than in the case of the lignin in wood or other lignin preparations. In order to explain this fact, it was assumed that a condensation of substances of carbohydrate origin occurred at the 5th position of the nucleus during the digestion, resulting in the increase of the frequency of the nucleus of type II. According to Csellak[3], the yield of vanillin from thiolignin by nitrobenzene oxidation is lower, when compared to that from the lignin in wood or the other types of lignin preparations. The yield of vanillin and syringaldehyde from Meadol by cupric oxide oxidation or oxidation with Fehling solution is also lower, when compared to that from lignosulphonic acid[4]. According to Leopold, model compounds having such nucleus as ((I) (R=H)), except those belonging to diphenyl methane type (III) or to pinoresinol type (IV), give vanillin in very high yield on oxidation with nitrobenzene[5]. The fact, that the yield of vanillin is lower in thiolignin in spite of its rather high content of phenolic hydroxyl group, suggests us, to together with the results of Richtzenhain, that thiolignin contains nuclei of type ((II) (R=H)) in rather high frequency.



I II III IV

As the yield of veratric acid and isohemipinic acid from the methylated lignin preparations by permanganate oxidation is supposed to be far from quantitative, and the yield of vanillin from thiolignin is expected to be very much influenced by the presence of carbonyl group[5] or of carboxyl group directly connected to benzene nucleus, it seems to be very interesting to estimate the frequency of the nucleus of type I (R=H) and II (R=H) by a quite different method. As will be stated later, Mannich reaction was used to differentiate both types of phenolic hydroxyl groups and the ratio of the amount of the phenolic hydroxyl groups belonging to these two types were found to be 25–40% and 75–60% respectively. If one can assume, according to Leopold[5], the ratio of (I) and (II) of the lignin in wood as 50 to 50%, one must probably admit the slight increase of (II) during the kraft cooking. It seems, however, incorrect to explain the low yield of vanillin from thiolignin by nitrobenzene oxidation by the increase of the condensed nucleus alone. It seems also to be important that thiolignin contains a carbon atom of higher oxidation stage directly connected to the nucleus, i.e. carbonyl group and carboxyl group, as was reported in the previous communication[1].

Estimation of the Amount of the Non-etherified Simple Guaiacyl Nucleus in Thiolignin

Mannich reaction on phenols, especially with dimethylamine, has been investigated rather much and the investigations done until 1942 are summarized by Blicke[7]. Among them, however, there is only guaiacol as phenols having a close connection to lignin, i.e. with guaiacyl nucleus. In general,

1) Part XIV, This Bulletin. **29**, 254 (1956).
2) H. Richtzenhain, *Svensk Papperstidn.*, **53**, 644 (1950).
3) W. Csellak, *Tappi.*, **34**, 472 (1951).
4) I. Pearl, *J. Am. Chem. Soc.*, **64**, 1429 (1942).
5) B. Leopold, *Svensk Kem. Tid.*, **64**, 18 (1952).
6) A. Wacek and K. Kratzl, *Cellulosechem.*, **20**, 108 (1942), *Ber.*, **76**, 891 (1943), *Ber.*, **77**, 516 (1944).
7) F. Blicke, "Organic Reactions", John Wiley & Sons, Inc., New York, Vol. I (1942), p. 303.

dimethylaminomethyl radical is introduced by Mannich reaction to ortho and para positions of the phenolic hydroxyl group.

As the phenolic hydroxyl groups of lignin belong mainly to type (I) and (II), it seems to be possible to estimate the amount of the former type with Mannich reaction, if it is confirmed by many model phenols that only those having the former nucleus react with formalin and dimethylamine under the condition of Mannich reaction. As will be stated later, experiments with model compounds revealed that 1) model compounds of type (I) give, without exception, Mannich base with substituent at 5th position in very high yield, 2) those of type (II) do not react, 3) carboxyl group having phenolic hydroxyl group in its para position is split off as carbon dioxide and dimethylaminomethyl group is introduced to the same position, 4) methylol group having phenolic hydroxyl group in its para position reacts with dimethylamine resulting in a formation of dimethylaminomethyl group at the same position, 5) other groups remain intact even when phenolic hydroxyl group exists in the para position, and 6) no reaction occurs when the phenolic hydroxyl group is etherified.

Since it is possible to estimate the amount of the carboxyl group, as reported previously[1], and the benzyl alcoholic group can be sulphonated at neutral pH to the sulphonic acid group, a group which does not react under the condition of Mannich reaction, it seems possible to estimate the amount of the phenolic hydroxyl groups belonging to type (I) and (II) (R=H) by Mannich reaction with dimethylamine.

When treated with formaldehyde and dimethylamine, the N/OCH_3 values of the thiolignin, which was used in the previous communication[1], increase along the curve I of Fig. 1. Saturation of the reaction is very good and about 0.35 atom nitrogen was introduced per methoxyl group after one to two days nitrogen content remaining constant even after prolonged reaction. Detailed analytical values are listed in the table.

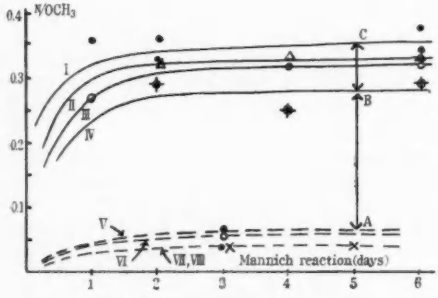


Fig. 1. N/OCH_3 values of thiolignin preparations after Mannich reaction with dimethylamine (D) or with piperidine (P). I Thiolignin (D), II Raney-Ni (D), III $NaBH_4$ (D), IV Sulphonation (D), V CH_2N_2 (D), VI $NaBH_4$, CH_2N_2 (P), VII CH_2N_2 (P), VIII Dioxanelignin CH_2N_2 (P).

Analytical Values of the Thiolignin Treated with Mannich Reaction.
(Analyzed in perchlorate form)

Reaction (days)	0	1	2	6
C%	61.33	55.12	56.36	56.51
H%	5.64	5.44	6.21	6.24
MeO%	15.31	12.56	13.05	12.95
S%	2.42			
N%	0.0	2.02	1.91	2.02
			2.10	2.22
N/MeO%	0.0	0.356	0.323	0.345
			0.356	0.379

Curves II and III, which show the N/MeO values of the thiolignin reduced with Raney alloy or with sodium borohydride respectively, followed by the treatment with Mannich reaction, are almost the same as Curve I. Curve IV is for the thiolignin sulphonated at neutral pH. This curve is lower than the Curves I, II or III. The difference BC seems to be due to the sulphonation of benzyl alcoholic group with phenolic hydroxyl group in its para position.

When thiolignin is once methylated with diazomethane, nitrogen must not be introduced by Mannich reaction. Curve V is for thiolignin methylated with diazomethane. Curves VI, VII and VIII are the N/MeO values of the thiolignin, thiolignin reduced with sodium borohydride and of the dioxane lignin used in the preceeding communication, after treating them with Mannich reaction using piperidine instead of dimethylamine. AB, obtained by subtracting this, so to say, blank value from the N/MeO value for the sulphonated thiolignin, corresponds to the amount of the nitrogen introduced to the unsubstituted fifth position and to the first position by displacing the carboxyl group.

As can be seem from the Fig. 2, the content of the phenolic hydroxyl group and the carboxyl group of the thiolignin used in these experiments are 0.4 and 0.18 per methoxyl group. Although it is unknown, how much of the carboxyl group has phenolic hydroxyl group in its para position, we may be allowed to assume, that about a half of the total carboxyl group has phenolic hydroxyl group in the para position, as the

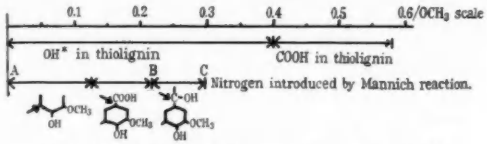


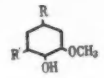
Fig. 2. Relation between the content of OH* and COOH groups thiolignin and the amount of nitrogen introduced by Mannich reaction.

thiolignin contains 0.4 phenolic hydroxyl group per methoxyl group, i.e. about one phenolic hydroxyl group per every two building units. If so, about one half of the total carboxyl group, i.e. 0.09 carboxyl group, may be displaced with dimethylaminomethyl group with Mannich reaction. Subtracting this amount from AB=0.22, the amount of the guaiacyl nucleus having no C–C bond at the fifth position may be obtained, the amount being calculated as 0.13 per methoxyl group. Admitting some uncertainty concerning the amount of the carboxyl group having free phenolic hydroxyl group in its para positon, it will be concluded that about 25–40% of the phenolic hydroxyl group of the thiolignin belongs to the simple guaiacol nucleus having no C–C bond at its fifth position.

Mannich Reaction on Lignin Model Compounds

Vanillin gives 5-dimethylaminomethyl vanillin (V) almost quantitatively by Mannich reaction with dimethylamine after one day. With piperidine, 5-piperidinomethyl vanillin (VI) was obtained in good yield. The structure of (V) was confirmed by synthesizing from it 5-formylvanillin (VII). At first, we attempted to lead (V) to (VII) with Thesing's method[8], i.e. to convert (V) to its methiodide (VIII) and then to oxidize the methiodide with nitrobenzene and phenylhydroxylamine to (VII). Although the methiodide was obtained in very good yield, the subsequent oxidation was unsuccessful. Snyder's method[9] was then attempted and found to be successful. 5-dimethylaminomethyl vanillin was reacted with hexamine in acetic acid and the product was hydrolyzed with water. 5-formylvanillin was obatined in the yield of 20%, which gave 5-carboxyvanillin with silver oxide oxidation, according to Pearl[10]. 5-Formylvanillin has been synthesized, according to Pearl, by nitrobenzene oxidation of 5-propenylvanillin, but the method was not so simple. Our method seems to be very convenient to synthesize 5-formylvanillin.

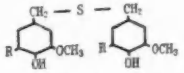
8) J. Thesing, *Ber.*, **87**, 507 (1954).
9) H. Snyder, S. Swaminathan and H. Sims, *J. Am. Chem. Soc.*, **74**, 5110 (1952).
10) I. Pearl, ibid., **74**, 4263 (1952).



R	R′
V –CHO	$-CH_2N(CH_3)_2$
VI –CHO	$-CHN(CH_2)_5$
VII –CHO	–CHO
VIII –CHO	$-CH_2N(CH_3)_3I$
IX $-COCH_3$	H
X $-COCH_2CH_3$	H
XI $-COCH_3$	$-CH_2N(CH_3)_2$
XII $-COCH_2CH_3$	$-CH_2N(CH_3)_2$
XIII $-CH_2CH_2CH_2$	H
XIV $-CH_2CH_2CH_2$	$-CH_2N(CH_3)_2$
XV $-CH_2SO_3\frac{1}{2}Ba$	H
XVI $-CH_2SO_3\frac{1}{2}Ba$	$-CH_2N(CH_3)_2$
XXI $-CH_2N(CH_3)_2$	$-OCH_3$
XXII $-CH_2N(CH_3)_2$	$-CH_2N(CH_3)_2$
XXIII $-CH_2OH$	$-CHN(CH_2)_5$
XXIV $-CHN(CH_2)_5$	$-CHN(CH_2)_5$

Acetovanillone (IX) and propiovanillone (X) gave 5-dimethylaminomethyl derivatives (XI) and (XII) respectively. Although it is known that some methylene group adjacent to carbonyl group reacts under some condition of Mannich reaction, Mannich base derived from acetovanillone (XI) was iodoform test positive (existence of -COMe) and Millon reaction negative (nonexistence of phenolic hydroxyl group with unsubstituted ortho position) and the Mannich base derived from propiovanillone (XII) was Millon reaction negative. As the iodoform tests of (V) and (XII) were negative and Millon reaction of (V) was negative and those of vanillyl sulphonic acid (XV) and guaiacol were positive, these color reactions seem to be effective for Mannich bases, too. The side chains of acetovanillone and propiovanillone may, therefore, remain intact during the Mannich reaction.

Propylguaiacol (XIII) and vanillyl sulphonic acid (XV) gave also 5-dimethylaminomethyl derivatives (XIV) and (XVI) in good yield under the same condition. Divanillyl monosulphide (XVII) gave Mannich base (XVIII) with two dimethylaminomethyl groups at its two unsubstituted fifth positions.



XVII R=H
XVIII R=$CH_2N(CH_3)_2$

Mannich base (XX) derived from dihydrodehydro-diisoeugenol (XIX) could not be obtained in crystalline form, but the analytical values of the perchlorate, obtained as a glassy substance, revealed that one dimethylaminomethyl group was introduced to the substance. As can be seen from the Fig. 3,

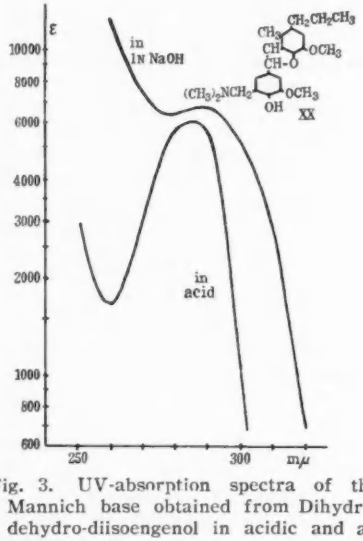
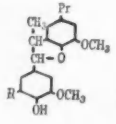


Fig. 3. UV-absorption spectra of the Mannich base obtained from Dihydrodehydro-diisoengenol in acidic and alkaline media.

the UV-absorption spectrum of the Mannich base is very similar to that of the starting material and it is concluded, from the difference of its alkaline spectrum and acidic spectrum, that the base is a monovalent phenol. For that reason, it may be concluded, that the phenyl-coumaran structure remains intact during the reaction and the dimethylaminomethyl is introduced only to the unsubstituted fifth position.



XIX R=H
XX R=$CH_2N(CH_3)_2$

Syringic acid gave Mannich base (XXI) with simultaneous decarboxylation of the carboxyl group. This base was converted to syringaldehyde by the Snyder's method, which was mentioned before. The yield of the syringaldehyde was rather low, but if it is possible to increase the yield by changing the reaction condition, this method may provide a very convenient way to synthesize syringaldehyde from gallic acid.

Mannich reaction with dimethylamine on vanillyl alcohol gave, after one day, picrate of Mannich base melting at 164–5°, with dimethylamino groups both at the fifth position and at the position of the methylol group (XXII). With piperidine, only the fifth position reacted even after four days, the picrate having the m. p. 153–4° (XXIII) being obtained. The yield was good in both cases.

With dimethylamine, vanillic acid gave Mannich base (XXII) having the m. p. of the picrate 164–5° after six days, which was found to be the same with the picrate obtained from vanillyl alcohol. The reaction must, therefore, involve the substitution under replacement of the carboxyl group, as well as the substitution at the fifth position. After only one day a picrate having the m. p. 175.5–176.5° was obtaind. No structural formula having the same analytical values with this compound was however found.

Mannich reaction with piperidine on vanillic acid during four days gave mannich base (XXIV) with simultaneous decarboxylation and substitutions at the fifth position and the position of the carboxyl group, the m. p. of the picrate being 204.5–5.5°. Mannich reaction during one day gave this picrate and that having the m. p. 209–210°. No structural formula for the latter picrate corresponding to the analytical values was however found. The structure of this unknown picrate seems to be analogous with that having the m. p. 175.5–176.5° obtained with dimethylamine.

Experimental

Mannich Reaction on Vanillin with Dimethylamine.—A mixture of vanillin (18.3 g.), 25% dimethylamine (64.8 ml.) and 30% formaldehyde (30 ml.) was set aside overnight, concentrated repeatedly in order to expel dimethylamine by adding water and then concentrated nearly to dryness. The separated yellowish-colored crystal was recrystallized from normal butanol. Product from the first recrystallization gave correct m.p. 138–139°, 15 g.

Anal. Found: C, 63.28; H, 7.14. Calcd. for $C_{11}H_{15}O_3N$ (V): C, 63.14; H, 7.23%.

The yield of the melting point pure picrate, obtained by adding picric acid to the reaction mixture obtained in the same reaction condition as above, was 95%, m.p. of the picrate 190.5–192°.

Anal. Found: C, 46.5; H, 4.18; N, 13.0; MeO, 7.32. Calcd. for $C_{17}H_{18}O_{10}N_4$ (picrate of V): C, 46.6; H, 4.12; N, 12.8; MeO, 7.08%.

Perchlorate, m.p. 207–208°.

Anal. Found: C, 42.81; H, 5.11; N, 4.47; Cl, 11.52. Calcd. for $C_{11}H_{16}O_7ClN$ (perchlorate of V): C, 42.8; H, 5.18 N, 4.53; Cl, 11.3%.

Mannich Reaction on Vanillin with Piperidine.—Vanillin (18.3 g.), acetic acid (200 ml.), piperidine (30 ml.) and 30% formalin (30 ml.) were mixed and allowed to stand at room temperature overnight. Acetic acid was distilled off in vacuo, sulphuric acid (20 g.) diluted with water added, and the acetic acid was expelled as compietely as possible. An appropriate amount of a dilute sodium hydroxide solution was added to make piperidine and the reaction product free, and the mixture was concentrated. The separated reaction product, which is contaminated by inorganic salt, was filtered, extracted with hot benzene, the benzene solution dried, and the product was crystallized from the benzene solution by adding ligroin and keeping in a refrigerator. After reprecipitation from its benzene solution by ligroin, the slightly brownish-colored 5-piperidinomethyl vanillin melted at 127–128.5°, 16.2 g.

Anal. Found: C, 67.30; H, 7.50. Calcd. for $C_{14}H_{20}O_3N$ (VI): C, 67.44; H, 7.68%.

Perchlorate, m.p. 212–213.5°C.

Anal. Found: C, 48.26; H, 5.58; N, 4.02; Cl 10.15; MeO, 9.28. Calcd. for $C_{14}H_{20}O_7NCl$ (perchlorate of VI): C, 48.2; H, 5.73; N, 4.02; Cl 10.0; MeO, 8.94%.

Picrate, m.p. 163–164°.

Anal. Found: C, 50.2; H, 4.60; N, 11.7. Calcd. for $C_{20}H_{22}O_{10}N_4$ (picrate of VI): C, 50.2; H, 4.60; N, 11.7%.

5-Dimethylaminomethyl Vanillin Methiodide.—5-Dimethylaminomethyl vanillin was shaken with methyl iodide, set aside over-night, petroleum ether added and the product was filtered. The iodide, m.p. 188–192° decomp., which was obtained nearly quantitatively, was dissolved in ethanol, which contained a little water, precipitated with ether, the m.p. being raised to 200–201° (decomp.).

Anal. Found: C, 40.97; H, 5.04; N, 3.76. Calcd. for $C_{12}H_{18}O_3NI$ (VIII): C, 41.0; H, 5.12; N, 3.99%.

Synthesis of 5-Formylvanillin from 5-Dimethylaminomethyl Vanillin.—A mixture of 5-dimethylaminomethyl vanillin (4.3 g.), hexamethylenetetramine (3.0 g.) and acetic acid (13 ml.) was boiled for five minutes, poured into water (130 ml.) and extracted repeatedly with ether. The etherial extract was shaken with dil. NaOH and the alkaline extract was acidified with dil. acid and kept in a refrigerator overnight. The separated crystal (0.8 g.), which melted at 115–118°, was filtered and recrystallized from xylol-ligroin, the m.p. being raised to 120–122° after one recrystallization

Anal. Found: C, 60.0; H, 4.35. Calcd. for $C_9H_8O_4$ (VII): C, 60.0; H, 4.4%.

5-Formylvanillin thus obtained gave 5-carboxyvanillic acid, m.p. 176–177°, by silver oxide oxidation according to Pearl[10].

Anal. Found: C, 50.66; H, 3.85. Calcd. for $C_9H_8O_5$: C, 50.9; H, 3.8%.

Mannich Reaction on Acetovanillone with Dimethylamine.—One gram of acetovanillone was dissolved in 25% dimethylamine (8 ml.), and 35% formalin (4 ml.) was added and the mixture was kept at room temperature overnight. Water was added and the picrate was precipitated by adding an alcoholic solution of picric acid. 3.3 g. of crude picrate, m.p. 166–170°, thus obtained, was recrystallized from 70% alcohol to give 2.0 g. of the pure picrate melting at 175–176°, yield 73.5%.

Anal. Found: C, 48.17; H, 4.63; N, 12.1. Calcd. or $C_{18}H_{20}O_{10}N_4$ (picrate of XI): C, 47.8; H, 4.43; N, 12.4%.

Mannich Reaction on Propioguaiacone with Dimethylamine.—Propioguaiacone (1 g.), synthesized according to Nakazawa[11], was dissolved in 25% dimethylamine (4 ml.), and 35% formalin (2 ml.) was added and the mixture was kept at room temp. overnight. Water was added and the picrate was precipitated by adding an alcoholic solution of picric acid. 3.3 g. of crude picrate, m.p. 155–157°, thus obtained, was recrystallized from 70% alcohol to give 2.2 g. of pure picrate melting at 160.5–161.5°, yield 85%.

Anal. Found: C, 49.33; H, 4.99; N, 11.8. Calcd. for $C_{19}H_{22}O_{10}N_4$ (picrate of XII): C, 49.0; H, 4.72; N, 12.0%.

Mannich Reaction on Cörulignol with Dimethylamine.—Cörulignol (XIII) (1 g.) was dissolved in 25% dimethylamine (4 ml.), and 35% formalin (2 ml.) was added and the mixture was kept at room temperature overnight. Water was added and the solution was acidified with dilute hydrochloric acid and extracted with ether. An alcoholic solution of picric acid was added in excess to the aqueous solution and the picrate, which separated as an oil was rubbed with a little amount of toluene to give 2.5 g. of crude picrate, m.p. 116–119°. 2.0 g. of the pure picrate was obtained from propyl alcohol, m.p. 120–121° yield, 74%.

Anal. Found: C, 50.7; H, 5.44; N, 12.6. Calcd. for $C_{19}H_{24}O_9N_4$ (picrate of XIV): C, 50.5; H, 5.31; N, 12.4%.

Mannich Reaction on Vanillyl Sulphonic Acid with Dimethylamine.—Barium salt of vanillyl sulphonic acid (0.5 g.) was dissolved in a mixture of 25% dimethylamine (2 ml.) and 35% formalin (1 ml.), and the mixture was kept at room temperature overnight, poured into alcohol and the precipitated barium salt was washed well with alcohol and analyzed.

Anal. Found: C, 37.40; H, 5.02; N, 3.87; S, 9.6; Ba, 20.7, Calcd. for $C_{11}H_{16}O_5NS\frac{1}{2}Ba$ (XVI): C, 38.55; H, 4.67; N, 4.08; S, 9.32; Ba, 19.9%.

Mannich Reaction on Divanillyl Monosulphide (XVII) with Dimethylamine.—Divanillyl monosulphide synthesized previously[12] (1.0 g.) was dissolved in a mixture of 25% dimethylamine (8 ml.) and 35% formalin (4 ml.), and kept at room temperature for four days. The solution was diluted with water, acidified with dilute hydrochloric acid and the separated starting material (0.3 g.) was recovered by filtration. Alcoholic solution of picric acid was added to the filtrate, and the picrate precipitated as an oil was washed with water and crystallized with alcohol to give 1.4 g. of pure picrate, melting at 179–180°.

11) K. Nakazawa, *J. Pharm. Soc. Japan*, **74**, 836 (1954).

12) H. Mikawa, This Bulletin, **27**, 50 (1954).

0.3 g. of the melting point pure picrate was recovered from the mother liquor, total yield 1.7 g.

Anal. Found: C, 46.63; H, 4.69. Calcd. for $C_{74}H_{98}O_{18}SN_{10}$ (picrate of XVIII): C, 46.5, H, 4.35%.

Mannich Reaction on Dihydro-dehydro-diisoeugenol (XIX) with Dimethylamine.—Dihydro-dehydro-diisoeugenol (0.2 g.) was dissolved in a mixture of 25% dimethylamine (0.4 ml.), 35% formalin (0.2 ml.) and 70% alcohol (1 ml.) and kept at room temperature overnight. On adding water to the solution, white precipitate separated, and this dissolved completely when dilute hydrochloric acid was added. Perchlorate was separated by perchloric acid, which did not crystallize.

Anal. Found: C, 57.99; H, 7.14; N, 3.06. Calcd. for $C_{23}H_{31}O_4N \cdot HClO_4$ (perchlorate of XX): C, 56.9; H, 6.59; N, 2.88%.

Mannich Reaction on Syringic Acid with Dimethylamine.—Syringic acid (1.5 g.) was dissolved in a mixture of 25% dimethylamine (6 ml.) and 35% formalin (3 ml.), was kept for four days at room temperature, diluted with water (100 ml.), and acidified with 2N hydrochloric acid; then an alcoholic solution of picric acid was added. The alcohol was distilled off in vacuo, and the separated picrate was filtered and washed with water. The crude picrate (3.2 g.) was recrystallized from aqueous alcohol to give 2.0 g. of melting point pure picrate, yield 60%.

Anal. Found: C, 46.55; H, 4.56; N, 12.60. Calcd. for $C_{17}H_{20}O_{10}N_4$ (picrate of XXI): C, 46.36; H, 4.58; N, 12.72%.

Syringaldehyde from 5-Dimethylaminomethyl-1, 3-Dimethylpyrogallol (XXI).—One gram of the picrate was dissolved in 50% aqueous acetone, passed through a column of an ion exchange resin IR 400 in bicarbonate form, acetone and water were distilled off in vacuo and the free base thus obtained was dissolved in the mixture of acetic acid (1.5 ml.) and hexamethylenetetramine (0.32 g.). The mixture was heated in an oil bath (115°) for five minutes, water was added and the mixture was extracted with ether. From the ether extract 50 mg. of melting point pure syringaldehyde was obtained by sublimation, yield 13%.

Mannich Reaction on Vanillyl Alcohol with Dimethylamine.—A mixture of vanillyl alcohol (1 g.), 25% dimethylamine (12 ml.) and 35% formalin (6 ml.) was kept at room temperature overnight, diluted with water, acidified and the picrate was precipitated with an alcoholic solution of picric acid. The precipitate was washed with water and recrystallized from aqueous alcohol to give 0.9 g. of pure dipicrate, melting at 164–165°.

Anal. Found: C, 42.26; H, 4.47; N, 16.2, 16.0. Calcd. for $C_{25}H_{29}O_{16}N_8$ (picrate of XXII): C, 42.1; H, 4.16; N, 16.1%.

Mannich Reaction on Vanillyl Alcohol with Piperidine.—Vanillyl alcohol (0.5 g.) was dissolved in a mixture of piperidine (0.8 ml.), 35% formalin (1 ml.) and alcohol (2 ml.), and the solution was kept at room temperature for four days, diluted with water, and acidified with dilute hydrochloric acid; alcoholic solution of picric acid was added and concentrated in vacuo. The separated crystalline picrate was recrystallized from aqueous alcohol to give 1.0 g. of pure picrate melting at 153–154°.

Anal. Found: C, 49.60; H, 5.12; N, 11.60. Calcd. for $C_{20}H_{24}O_{10}N_4$ (picrate of XXIII): C, 50.0; H, 5.0; N, 11.65%.

Mannich Reaction on Vanillic Acid with Dimethylamine.—Vanillic acid (1.1 g.) was dissolved in a mixture of 25% dimethylamine (4 ml.) and 35% formalin (2 ml.), and kept at room temperature for six days. The solution was poured into 10 ml. of water and acidified with dil. hydrochloric acid. Alcoholic solution of picric acid was added and the alcohol was evaporated in vacuo. The separated picrate was recrystallized from aqueous alcohol, m.p. 165.5–167°. No melting point depression was observed on admixture with the picrate XXII, m.p. 164–166°, obtained from vanyllyl alcohol. Marked melting point depression was observed, however, on admixture with the picrate, m.p. 175.5–176.5°, which was obtained by Mannich reaction on vanillic acid during only one day. Yield 2.7 g.

The crude picrate obtained at the same reaction conditions but after only one day gave a picrate, m.p. 175.5–176.5°, after recrystallization from dilute alcohol. From the mother liquor 0.2 g. of the same substance was further recovered. Total 0.95 g. No other substances were obtained. (Found: C, 45.21; H, 4.48; N, 11.73%). No structural formula corresponding to these analytical values was found.

Mannich Reaction on Vanillic Acid with Piperidine.—Vanillic acid (1.1 g.) was dissolved in a mixture of piperidine (1.7 ml.), 35% formalin (2 ml.), water (3.3 ml.) and alcohol (4 ml.), and kept at room temperature overnight, poured into water and an alcoholic solution of picric acid was added. On recrystallization of the crude picrate from dilute alcohol, two different picrates having m.p. 204.5–205.5° and 209–210° were obtained. The former one, 1 g., which is comparatively sparingly soluble needles, was analyzed as follows.

Anal. Found: C, 47.5; H, 4.57; N, 14.1. Calcd. for $C_{31}H_{35}O_{16}N_8$ (picrate of XXIV): C, 47.9; H, 4.64; N, 14.4%.

The latter picrate, 1 g., which is comparatively easily soluble, showed the following analytical values, but no structural formula having these values were found

(Found: C, 43.11, 43.88, 43.72; H, 3.51, 3.49, 3.74; N, 13.65, 12.83; MeO, 4.5%).

This picrate with unknown structure disappeared when the Mannich reaction was performed four days at the same condition, picrate having the m.p. 204.5–205.5°, XXIV, being the only product obtained. Yield, 1.6 g.

Mannich Reaction on Thiolignins.—Various thiolignin preparations used in this communication are the same with those prepared in the previous communication[1]. When dimethylamine was used, 0.5 g. of lignin was dissolved almost completely in a mixture of 25% dimethylamine (4 ml.) and 35% formalin (2 ml.), and set aside at room temperature. When piperidine was used, 0.2 g. of lignin was dissolved in 2 ml. of piperidine solution (a mixture of piperidine (5 ml.), 35% formalin (6 ml.) and alcohol (12 ml.)), and the solution was

kept at room temperature. After the reaction, the solution was poured into an excess of 2N hydrochloric acid, and the coagulated lignin was filtered and washed with water. The lignin was then dissolved in a little amount of acetone, poured into a dilute solution of perchloric acid and the precipitated lignin was filtered and washed with perchloric acid. The precipitate was redissolved in acetone and reprecipitated with perchloric acid in the same manner. After the lignin was washed well with perchloric acid, it was washed with water, ether-alcohol 1: 1, ether and then with petroleumether.

Summary

Mannich reactions on many lignin model compounds revealed that 1) model compounds of type (I) give without exception Mannich base with substituent at fifth position in very high yield, 2) those of type (II) do not react, 3) carboxyl group having phenolic hydroxyl group to its para position is split off as carbon dioxide and dimethylaminomethyl group is introduced to the same position, 4) methylol group having phenolic hydroxyl group to its para position reacts with dimethylamine resulting in the formation of dimethylaminomethyl group at the same position, 5) other groups remain intact even when phenolic hydroxyl group exists in para position, and 6) no reaction occurs when the phenolic hydroxyl group is etherified.

By applying the Mannich reaction with dimethylamine on thiolignin, it has been concluded that about 25–40% of the phenolic hydroxyl group of thiolignin belongs to the simple guaiacol nucleus of type (I) having no C-C bond at its fifth position, admitting some uncertainty concerning the amount of carboxyl group having free phenolic hydroxyl group in its para position.

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Studies on the Cooking Mechanism of Wood. XVI[1]*. On the Mechanism of Kraft Cooking*

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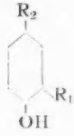
Hydrogen Sulphide Cooking of α-Guaiacyl Propanol

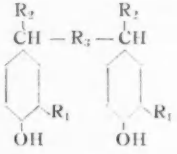
Hägglund and Enkvist found that the lignin in wood combines with sulphur, when the wood is cooked by a neutral aqueous solution of hydrogen sulphide at 100°[2]. This so-called hydrogen sulphide cooking was thought by them to represent the initial reaction of the ordinary kraft cooking. It was shown by us, that the sulphur, introduced to lignin by the hydrogen sulphide cooking, combined with the so-called X group of the lignin[3], a group which was most easily sulphonatable by a neutral sulphite solution. The structure of this group is now believed to be benzyl alcohol or benzyl ether group with free phenolic hydroxyl group in its para position[3,4]. It is, therefore, very important for the elucidation of the mechanism of the kraft cooking reaction, to investigate the behavior of the model compounds for the X group toward hydrogen sulphide cooking. Among others[5], only vanillyl alcohol (I), *p*-hydroxybenzyl alcohol (II) and its ethers are investigated in some detail by Enkvist[6] and ourselves[7]. It has been shown, that they gave the corresponding monosulphide (III, IV) and disulphide (V), while recently Zentner[8] reported that α-guaiacyl propanol (VI) gave only its dehydrated product, isoeugenol, under the condition of the ordinary

1) Part XV, This Bulletin, **29**, 259 (1956).
2) a) E. Hägglund, *Svensk Papperstidn.*, **44**, 183 (1941); b) T. Enkvist, M. Moilanen and B. Alfredsson, *Svensk Papperstidn.*, **52**, 517 (1949).
3) H. Mikawa, K. Sato, C. Takasaki and H. Okada, *J. Chem. Soc. Japan (Ind. Sect.)*, **54**, 299 (1951); H. Mikawa, ibid., 651.
4) B. Lindgren, *Acta Chem. Scand.*, **5**, 603 (1951).
5) T. Enkvist and M. Moilanen, *Svensk Papperstidn.*, 55, 668 (1952).
6) T. Enkvist and M. Moilanen, *Svensk Papperstidn.*, 52, 183 (1949).
7) H. Mikawa, This Bulletin **27**, 50. 53 (1954).
8) T. Zentner, *Tappi.*, **36**, 517 (1953)

hydrogen sulphide cooking. It seemed, therefore, to be quite important to reinvestigate the propanol with special attention to the sulphur containing reaction products, if any.



	R_1	R_2
I	OCH_3	$-CH_2OH$
II	H	$-CH_2OH$
VI	OCH_3	$-CH(OH)C_2H_5$
IX	OCH_3	$-CHO$
X	OCH_3	$-CH_2SH$
XI	OCH_3	$-CHS$



	R_1	R_2	R_3
III	OCH_3	H	$-S-$
IV	H	H	$-S-$
V	OCH_3	H	$-S-S-$
VII	OCH_3	$-C_2H_5$	$-S-S-$
VIII	OCH_3	$-C_2H_5$	$-S-$

Reaction products obtained from the α-guaiacyl propanol by the hydrogen sulphide cooking at 100° during six hours, gave four spots by paper chromatography, those of unreacted propanol, bis-(1-(4-hydroxy-3-methoxyphenyl)-1-propyl) disulphide (VII), bis-(1-(4-hydroxy-3-methoxyphenyl)-1-propyl) monosulphide (VIII) and some unknown compound. The separation of these compounds in larger scale was performed by developing the product adsorbed on a Florizil column with benzene. The disulphide, thus separated, showed no melting point depression on admixture with the product synthesized according to Zentner[8]. The monosulphide was separated as dibenzoate and its structure was determined from the analytical values and the molecular weight measured according to Rast's method.

Thus confirming the formation of mono- and disulphide also from α-guaiacyl propanol, the mechanism of the formation of monosulphide and disulphide from *p*-hydroxybenzyl alcohols by hydrogen sulphide cooking discussed in the previous communication[7] seems to be applicable in general.

Alkaline Decomposition of Vanillyl Monosulphide (III)

The sulphur introduced to lignin by hydrogen sulphide cooking was partly split off by the treatment with alkali at 160°[2b,9], resulting in a formation of thiolignin with rather low content of sulphur, thus explaining why the sulphur content of the thiolignin isolated from the black liquor of the industrial cooking was comparatively low.

Enkvist investigated the behavior of vanillyl disulphide (V) against alkali, as the model for the "hydrogen sulphide lignin". He confirmed the fact that the disulphide sulphur was split as hydrogen sulphide, resulting in a formation of vanillin[2b]. The stability of the disulphide sulphur of this model compound was, however, much lower than the sulphur contained in the hydrogen sulphide lignin. The alkaline decomposition of 4,4'-dihydroxydibenzyl monosulphide (IV) and of vanillyl monosulphide (III), synthesized by us, was investigated previously very briefly[7]. The latter compound was investigated also by Enkvist spectroscopically[10]. These monosulphides were found to be much more stable against hot alkali than the disulphide, although they also split sulphur as hydrogen sulphide just as in the case of vanillyl disulphide and hydrogen sulphide lignin. As it seems to be very important to know the decomposition products of the vanillyl monosulphide against hot alkali, the behaviour of this compound was investigated rather precisely in the present communication.

Vanillyl monosulphide was decomposed with 5% alkali and the products were examined by paper chromatography. A spot for the starting monosulphide was too strong even after heating for six hours at 120° as yet and the decomposition condition of three hours at 130° was found to be suitable for the investigation of the products. The chromatogram was not so simple, and the materials which were isolated as crystals and identified by mixed melting point determinations, were unreacted starting monosulphide, vanillin and vanillyl alcohol. By comparing the chromatogram with that of the products of the alkaline decomposition of vanillyl alcohol alone, however, almost all of the unidentified spots were found to be due to the secondary reaction products of vanillyl alcohol. Only one spot remained

9) T. Enkvist, *Svensk Papperstidn.*, **51**, 225 (1948); T. Enkvist and E. Hägglund, *Festskr. J. A. Hedvall*, 149 (1948).

10) J. Lindberg and T. Envist, *Societas Scientiarum Fennica Commentationes Physico-Mathematicae* (1953), XVII, 4.

unidentified, which corresponded to the direct decomposition product of the vanillyl monosulphide. The decomposition proceeds, therefore, as follows: $III \rightarrow IX + I + (I)_x + SH^-$.

As stated above, Enkvist investigated spectroscopically the decomposition of vanillyl monosulphide at 100°. Comparing the UV-absorption spectrum of vanillyl monosulphide and its decomposition products and from the vanillin odor of the product, he assumed that some amount of vanillin may be formed by the alkaline decomposition of the monosulphide. From the fact that the adsorption maximum of the monosulphide at 284 mμ shifts 4 mμ to the shorter wave-length side after the alkaline decomposition, he pointed out also the possibility that the monosulphide was degraded to smaller molecules, possibly to vanillyl alcohol or to vanyllyl mercaptan. From these considerations he assumed the mechanism of the decomposition of the monosulphide as follows: $2III \rightarrow X + I + XI$, $XI \rightarrow IX + SH^-$.

In so far as the reaction products are concerned, the mechanism agrees rather well with our findings. The fact that both monosulphide and disulphide, the products of the hydrogen sulphide cooking of the model compounds for the X-group, gave vanillin when decomposed with hot alkali, suggests to us that thiolignin contains carbonyl group at the same position, where the X-group was situated before the cooking.

On the Mechanism of the Kraft Cooking and the Structure of the Thiolignin

It was pointed out at first by Kullgren[11], that the combination of sulphur and lignin was the main reason why wood was delignified much more easily by the kraft cooking process than by the soda process. At the beginning of the ninteen forties, Hanson, Brauns and Ahlm investigated the sulphur atoms contained in the ordinary thiolignin, recovered from the black liquor[12]. All of them though that it was in the form of mercaptan. Hägglund and Enkvist, however, made clear that thiolignin contained mainly only monosulphide (thioether) sulphur[2]. They also showed that the sulphur contained in the hydrogen sulphide lignin was in monosulphide and disulphide form[2] and that this sulphur was partly split off by alkali at 160° resulting in the formation of the ordinary thiolignin.

As stated previously, it was shown by us that the sulphur introduced to lignin by the hydrogen sulphide cooking combined with the X-group of lignin[3] and the hydrogen sulphide cooking of the model compounds for the X-group were investigated in the present paper and by Enkvist[5,6] and ourselves[7]. They gave monosulphide and disulphide just as in the case of the hydrogen sulphide cooking of lignin. The alkaline decomposition of these compounds was also investigated not only in this paper but also by them[6,7,10] and it was found that the monosulphide sulphur was much more stable than the disulphide sulphur, although both of them were split as hydrogen sulphide. The behaviour of the hydrogen sulphide lignin against alkali was thus confirmed with the model compound.

The second important reaction involved in the kraft cooking process is the alkaline cleavage of the arylether linkages in the lignin. The content of the phenolic hydroxyl group of alkali lignin and thiolignin has been investigated by Marshall et al.[13], Brauns[14], Enkvist[15] and ourselves[16]. According to our data, the phenolic hydroxyl group of the lignin in situ, $0.14/CH_3O$ as was reported in Part XIII of this series, increased to $0.4/CH_3O$[16] after the kraft cooking, thus confirming the marked increase of the phenolic hydroxyl group during the digestion.

The cleavage of the ether linkage of lignin accompanies the degradation of its molecular size. The molecular weight of alkali lignin and thiolignin has been measured by a number of authors[17]. Almost all values are less than 1000 and some of them are so small as 400–500. The molecular weight determination of alkali lignin and thiolignin by the Rast method was investigated by us and it was concluded that the measurement must be made with the methylated or acetylated samples[18]. By this method, molecular weight distribution curves for alkali lignin and thiolignin were obtained and it was found that the molecular weight concentrated mainly around 1000 and 1500[19]. Enkvist reports also that the molecular weight lies

11) C. Kullgren, *Papierfabrikant*, **24**, 20 (1926).

12) F. Hanson, *Paper Trade J.*, **112**, No. 2, 32 (1941); F. Brauns, ibid., **111**, No. 14, 33 (1940); C. Ahlm, ibid., **113**, No. 13, 115 (1941).

13) H. Marshall, F. Brauns and H. Hibbert, *Can. J. Res.*, **13** B, 103 (1935).

14) F. Brauns and W. Grimes, *Paper Trade J.*, **108**, No. 11, 40 (1939).

15) T. Enkvist and B. Alfredsson, *Svensk Papperstidn.*, **54**, 185 (1951).

16) H. Mikawa, K. Sato, C. Takasaki and K. Ebisawa, This Bulletin, **29**, 254 (1956).

17) Y. Hachihama and S. Jodai, "Chemistry of Lignin", Nihonhyronsha, Tokyo (1946), p. 270; R. Glover and J. Bain, *Can. J. Res.*, **14** B, 65 (1936); Y. Hachihama and S. Jodai, *J. Soc. Chem. Ind. Japan*, **52**, 306 (1949); F. Lahey and J. Merewether, *Australian J. Sci. Res. Ser. A.*, **1**, 112 (1948).

18) H. Mikawa and H. Okada, *J. Chem. Soc. Japan, (Ind. Sec.,)* **54**, 239 (1951).

19) H. Mikawa, ibid., 150, 152.

mainly between 1000–1500[9].

The structure of the side chain of thiolignin has not been much investigated, especially in connection with the mechanism of the sulphidation of lignin and the subsequent splitting of the sulphur once introduced at the beginning of the kraft cooking by alkali. This problem was discussed rather precisely in the previous communication[18], and the existence of the carbonyl group and the double bond conjugated

Summarizing these findings mentioned above, one may be allowed to formulate the mechanism of the kraft cooking as follows (cf. Fig. 1): (1) At the beginning of the cooking, the X-group of the lignin in wood (XIV) reacts with sodium sulphide to give mercaptan (XV). The mercaptan reacts rapidly with the other hydroxyl group of the lignin to give monosulphide (XVI), while it is partly oxidized with some group of the lignin to the disulphide group (XVII). The

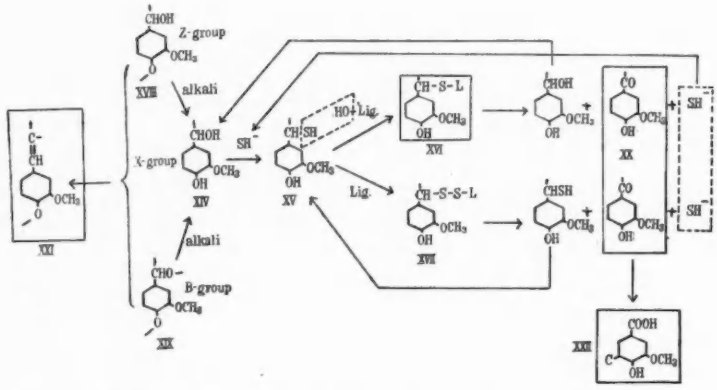
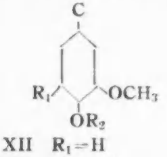


Fig. 1. Reactions of lignin during the kraft cooking.

with the benzene nucleus and the carboxyl group directly attached to the nucleus was concluded, and the mechanism involved in the formation of these group was also discussed.

The nuclear structure of thiolignin was investigated rather precisely by Richtzenhain[20] and also by us in the previous communication[1]. Richtzenhain proved the existence of the nuclei of type XII and XIII and showed the increase of the proportion of the latter nucleus during the kraft cooking. We showed that the proportion of XII(R_2=H) and XIII(R_2=H) was about 25–40% and 75–



XII R_1=H
XIII R_1=—C

60%, indicating that the nuclei belonging to the latter type increase a little during the cooking. This problem has been thoroughly discussed in the previous communication[1].

20) H. Richtzenhain, *Svensk Papperstidn.*, 53, 644 (1950).

lignin isolated at this stage is the hydrogen sulphide lignin obtained by the hydrogen sulphide cooking of wood. Until this stage, only the X-group enters into reaction and the sulphur contained in the hydrogen sulphide lignin is in both monosulphide and disulphide form.

(2) Next, the temperature rises in the presence of alkali and the cleavage of the ether linkage occurs. This cleavage of the ether linkage occurs also at the Z-group (XVIII) and B-group (XIX), resulting in a formation of the X-group, which reacts further to give monosulphide and disulphide just as in the case of (1). This cleavage of the ether linkage causes the splitting of the lignin molecule and the increase of the content of the phenolic hydroxyl group.

(3) At the same time, the disulphide group (XVII) is decomposed very easily with hot alkali to give the mercaptan, regenerating SH^- ion. A certain amount of carbonyl group conjugated with the nucleus (XX) is also formed. Monosulphide group (XVI) is much more stable than the disulphide group, but it is also partly decomposed with hot alkali to give carbonyl group (XX) at its position, while partly regenerating the X-

group and the SH^- ion.

(4) X, Z (XVIII) and B-groups (XIX), which are taking part in such complex reactions mentioned above, are on the other hand partly dehydrated by hot alkali to give double bond conjugated with the nucleus (XXI). The carbonyl group (XX) thus formed is converted partly to the carboxyl group (XXII) directly connected to the nucleus. Condensation reaction occurs to some extent at the same time resulting in an increase of the amount of the nuclei having C–C bond at the fifth position adjacent to the phenolic hydroxyl group.

(5) During these complicated reactions most of the very reactive X, Z and B-groups are kept in combination with sulphur, especially in the most stable monosulphide form. These groups are thus protected from the undesired condensation reason tion during the cooking. This is the main reason why the delignification is easier in kraft cooking than in the soda cooking. Thus, ultimately, thiolignin with a small amount of sulphur mainly in the form of the stable monosulphide having the molecular weight of about 1000–1500 dissolves out in alkali due to its carboxyl group and phenolic hydroxyl group.

Experimental

Hydrogen Sulphide Cooking of α-Guaiacyl Propanol (VI).—Hydrogen sulphide was bubbled through a Clark-Lubs buffer solution (100 ml.) (50 g. of KH_2PO_4 and NaOH in one liter of water, pH 7) until the concentration of hydrogen sulphide reaches 0.36 N, α-guaiacyl propanol (3 g.) added and the mixture was rotated in a stainless autoklave (150 ml.) for six hours at 100° in an oil bath.

The solution was extracted exhaustively with ether, ether was expelled, and the residue (3 g.) was tested chromatographically on a strip of the Toyo filter paper No. 50 buffered with Clark-Lubs buffer solution at pH 7 using benzene-petroleum ether 1:1 as a mobile phase. Four spots were observed by diazotized sulphanilic acid at Rf 1.0, 0.90, 0.79 and 0.52, of which the weak spot at Rf 0.52 was of the unreacted α-guaiacyl propanol.

The residue was kept in a refrigerator for two weeks and the separated crystal was filtered, washed with a mixture of benzene and petroleum ether and recrystallized from the same solvent mixture, m.p. 112–114.5°, 100 mg., Rf=0.79. This crystal did not show any melting point depression on admixture with the bis(1-(4-hydroxy-3-methoxyphenyl)-1-propyl) disulphide (VII), m.p. 115–116°, synthesized according to the method of Zentner[8].

Anal. Found: C, 61.58; H, 6.77; S, 16.32. Calc. for $C_{20}H_{26}O_4S_2$ (VII): C, 61.0; H, 6.59; S, 16.21%.

The filtrate from the crystal was concentrated, dissolved in benzene, adsorbed on a Florizil column (diameter 17 mm., length 270 mm.), developed at first with benzene, and the eluate was tested by paper chromatography. After the first fraction with Rf=1.0, 0.61 g., the second fraction, a mixture of two substances with Rf=0.90 and 0.79, 2.1 g., was obtained by eluting the column with a mixture of benzene and alcohol 9:1. The column was then washed with alcohol and a small amount of the third fraction consisting of only unreacted α-guaiacyl propanol was obtained.

The first fraction was crystallized as a benzoate having m.p. 154–155° from alcohol, 0.25 g. The analyses and the molecular weight obtained by the Rast method agree with the corresponding valueus of the dibenzoate of bis(1-(4-hydroxy-3-methoxyphenyl)-1-propyl) monosulphide (VIII).

Anal. Found: C, 71.4; H, 6.13; S, 5.7; OCH_3, 11.2; molecular weight (Rast), 630. Calc. for $C_{24}H_{34}O_6S$ (dibenzoate of VIII): C, 71.2; H, 5.93; S, 5.6; OCH_3, 10.8%; molecular weight, 574.6.

The second fraction containing the disulphide and an unknown compound with Rf=0.90 was not investigated further. The sulphur content of the fraction, 10.37%, was rather high.

Decomposition of Vanillyl Monosulphide (III) with Hot Sodium Hydroxide Solution.—Vanillyl monosulphide (1.5 g.) was dissolved in

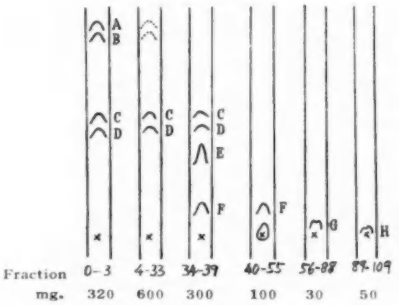


Fig. 2. Paper chromatograms of the products of alkaline decomposition of vanillyl monosulphide separated into 109 fractions by Al_2O_3 adsorption chromatograph, B: Vanillyl monosulphide, H; Vanillyl alcohol, D: ?, A, C, E, F, G: Secondary products of vanillyl alcohol.

5% sodium hydroxide (75 ml.), kept at 130° for three hours in an autoklave with nitrogen atmosphere, acidified with sulphur dioxide and extracted with ether. From the aqeous solution 2,4-dinitrophenyl hydrazone having m.p. 255–257° was obtained, 0.24 g. After recrystallization from dioxane the hydrazone did not show any melting point depression on admixture with the authentic vanillin 2,4-dinitrophenyl hydrazone.

The ether extract was concentrated, dissolved in benzene, adsorbed on a column of alumina (a mixture of 330 g. of active alumina and 33 g. of cellite, diameter 30 mm., length 580 mm.), developed with benzene and separated into 109 fractions. Paper chromatograms of these fractions are shown in Fig. 2. From the fractions O-3 vanillyl monosulphide was separated and identified

by mixed melting point determination, 100 mg. Fractions 89–109 contain only vanillyl alcohol, 50 mg. These chromatograms were compared with that of the product obtained by treating the vanillyl alcohol with sodium hydroxide just in the same condition as in the case of the vanillyl monosulphide and it was found that the spots A, C, E, F and G were those of the secondary products produced from the vanillyl alcohol by alkali. Although the substance corresponding to the spot D seemed to be the direct fission product of the vanillyl monosulphide, it was impossible to isolate it, as the intensity of C was very strong. Yield; recovered monosulphide 7%, vanillin 8%, vanillyl alcohol 4%. Almost all of the remaining part consisted of secondary products from vanillyl alcohol.

Summary

1. Hydrogen sulphide cooking of α-guaiacyl propanol (VI) gave bis(1-(4-hydroxy-3-methoxyphenyl)-1-propyl) monosulphide (VIII) and disulphide (VII).

2. Vanillyl monosulphide was decomposed with alkali at 130°. Vanillin, vanillyl alcohol and the secondary products from vanillyl alcohol were identified.

3. The mechanism of the kraft cooking process was discussed and a new mechanism was proposed.

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Heats of Dilution of Polystyrene Solutions. I

By Kazuo AMAYA and Ryoichi FUJISHIRO

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Introduction

It is well known that entropy plays an important role in defining thermodynamical behaviours of high polymer solutions. Enthalpy has also a great significane as an interaction parameter between polymer and solvent.

Enthalpy can be obtained from the temperature dependence of osmotic pressure or vapor pressure of polymer solutions, and such experiments were reported by various authors[1,2,3,4,5], but the data calculated from their results are not accurate. Direct measurements of heat of dilution of polymer solutions were reported by a few authors[3,7,8] but their results had a considerable error in the range of concentrations where the heat changes are small.

It is thought that a more accurate measurement of heat of dilution of various polymer solutions has a great significance in explaining the thermodynamical behaviours of polymer solutions.

We constructed a calorimeter using thermister capable of measuring temperature change down to 0.5×10^{-4}°C (0.003 cal.) and measured the heats of dilution of three polystyrene solutions, using toluene, ethylbenzene and chloroform as solvents.

Experimental

Apparatus and Procedure.—The calorimeter. The calorimeter, similar to those described by Gee[3] and Meares[7], but different from them in using a thermister, was constructed and is shown in Fig. 1.

A is an unsilvered Dewar vessel 21 cm. long and 3.5 cm. in inner diameter. A double bulb, consisting of the inner bulb B and the outer bulb C, is the mixing bulb. The polymer solution S to be diluted was introduced into the outer bulb C from a pipette with a long delivery tube which reached to the bottom through the inner bulb B, and was separated by a pool of mercury F from the solvent S′ which is in the inner bulb B. To minimize the evaporation loss of the solvent from the outer bulb a rubber ring D which was fixed to the inner bulb was fitted tightly with the

1) G. Gee and W.J.C. Orr, *Trans. Faraday Soc.*, **42**, 507 (1946).
2) M.J. Newing, ibid., **46**, 613 (1950).
3) C.E.H. Bawn, R.F.J. Freeman and A.R. Kamaliddin, ibid., **46**, 677 (1950).
4) M.J. Schick, P. Doty and B.H. Zimm, *J. Am. Chem. Soc.*, **72**, 531 (1950).
5) C.E.H. Bawn and M.A. Wajid, *J. Polymer Sci.*, **12**, 109 (1954).
6) J. Ferry, G. Gee and L.R.G. Treloar, *Trans. Faraday Soc.*, **41**, 340 (1945).
7) P. Meares, ibid., **47**, 699 (1951).
8) H. Tompa, *J. Polymer Sci.*, **8**, 51 (1953).

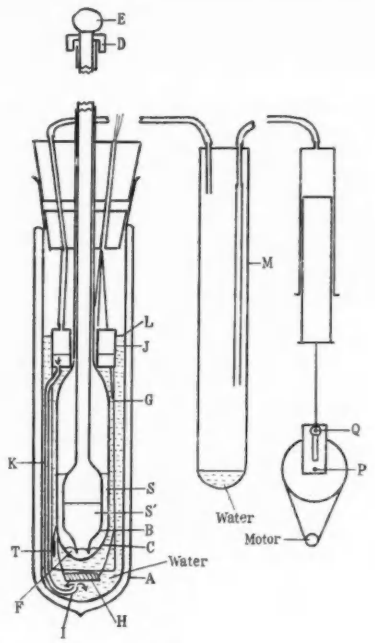

Fig. 1.

outer bulb. The inner bulb was closed by a rubber cap E at the top.

By raising the inner bulb and then moving it up and down in the solution, the solution was moved up and down through the aperture between the inner bulb and the outer bulb, and the mixing was performed. The polymer solution was fairly viscous, and sufficient mixing could not be achieved by only rotating the inner bulb.

The mixing bulb fitted centrally through a rubber bung into the Dewar vessel A filled with water up to the level L indicated in the diagram. A stirrer fitted with an injector was devised. The piston of the injector was connected to a rod R at Q which was rotated around the pivot P at a speed 20 r.p.m.. The volume of the air pumped in and out of the injector during a cycle was controlled by adjusting the distance between P and Q.

The exit of the injector was connected, through the water vapor saturator M, 270 cc. in volume, acting also as a temperature moderator, to a copper tube J in the Dewar vessel. J is a coaxial copper tube the inner tube of which was fitted loosely to C having holes at the upper and the bottom. To the hole at the bottom was connected a rubber tube K, the other end I of which reaches to the bottom of the Dewar vessel. By the motion of the piston of the injector the water in J going in and out through the rubber tube K and the water in the Dewar vessel was stirred.

To ensure immediate attainment of the thermal equilibrium, a piece of copper plate G, which almost covers the outer bulb C was connected to J. The calorimeter and the saturator were immersed in the water thermostat at 25°C kept constant to $\pm 1\times10^{-4}$°C.

The temperature changes were measured with a thermister T having about 400 KΩ in resistance and a temperature coefficient of −5.5 percent at 25°C. The heat capacity of the calorimeter was determined by introducing measured amounts of electrical energy through the constantan heater H having resistance of about 37 Ω. An electrical current passing through the heater was measured by a precision type m.A. meter, and the time during which the electrical current was passed was measured with a stop watch.

Various kinds of thermometer systems employing a thermister were tried. The most simple one, combining a low resistance thermister and a galvanometer was proved to be unsatisfactory because of the effect of self-heating of the thermister. The one employing a.c. Wheatstone bridge with a high resistance thermister and a.c. vacuum tube amplifier was quite satisfactory to eliminate the self-heating, but the adjustment of 2 components, namely resistance and capacitance was very cumbersome in the actual operation. The following was finally adopted.

The block diagram of the resistance measuring unit adopted is shown in Fig. 2. Unbalanced d.c. voltage across the Wheatstone bridge was converted to 30 c/s a.c. voltage by a converter driven by 30 c/s oscillator. The converter was made of a permanent dynamic speaker and was shown in Fig. 3. Converted signals were fed to a narrow band amplifier and to a phase sensitive detector. The output was detected by a μA meter

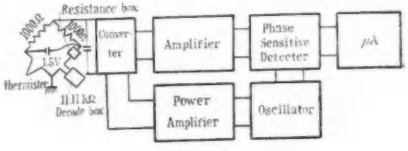

Fig. 2

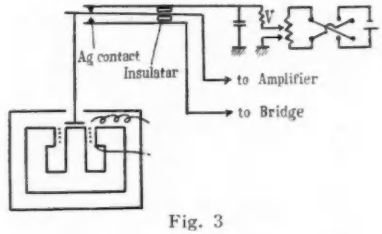

Fig. 3

and the resistance reading was performed by adjusting the resistance of the Wheatstone bridge so that the meter deflection returns to its zero point. The arms of the Wheatstone bridge were immersed in the thermostat except the 11.11 KΩ decade box.

The electrical circuits of the narrow band amplifier employing two twin-T. bridge is shown in Fig. 4. The phase sensitive detector is the same as that described by Schuster[9]. The oscillator and the driver of the converter are shown in Fig. 5 and Fig. 6 respectively.

1 Ω change in resistance can be detected. The resistance of the thermister is about 400 KΩ and

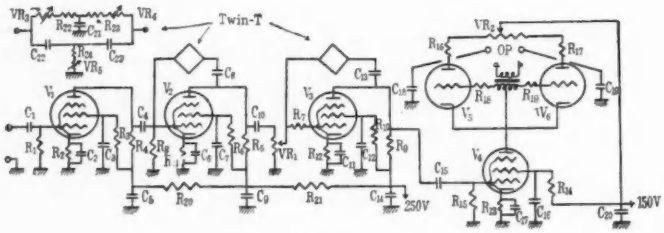

Fig. 4

R_1	100 KΩ	R_{13}	20 KΩ	C_2	100 μF	C_{16}	10 μF
R_2	2 KΩ	R_{17}	20 KΩ	C_3	2 μF (oil)	C_{17}	100 μF
R_3	1 MΩ	R_{18}	30 KΩ	C_4	0.1 μF	C_{18}	20 μF
R_4	500 KΩ	R_{19}	30 KΩ	C_5	20 μF	C_{19}	20 μF
R_5	500 KΩ	R_{20}	100 KΩ	C_6	100 μF	C_{20}	20 μF
R_6	1 MΩ	R_{21}	100 KΩ	C_7	3 μF	C_{21}	0.04 μF
R_7	2 MΩ	R_{22}	250 KΩ	C_8	0.1 μF	C_{22}	0.02 μF
R_8	2 MΩ	R_{23}	250 KΩ	C_9	20 μF	C_{23}	0.02 μF
R_9	500 KΩ	R_{24}	125 KΩ	C_{10}	0.1 μF	V_1	6SH7
R_{10}	1 MΩ	VR_1	1 MΩ	C_{11}	100 μF	V_2	6SH7
R_{11}	2 KΩ	VR_2	10 KΩ	C_{12}	3 μF	V_3	6SH7
R_{12}	2 KΩ	VR_3	100 KΩ	C_{13}	0.1 μF	V_4	6SH7
R_{13}	150 Ω	VR_4	100 KΩ	C_{14}	20 μF	V_5	1/2 6SN7
R_{14}	50 KΩ	VR_5	50 KΩ	C_{15}	0.1 μF	V_6	1/2 6SN7
R_{15}	500 KΩ	C_1	0.1 μF				

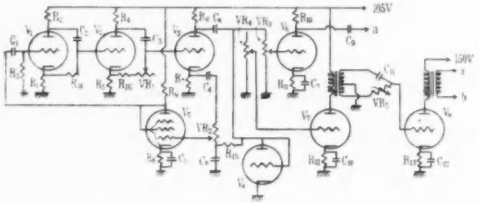

Fig. 5

R_1	1 KΩ	C_1	0.1 μF
R_2	1 KΩ	C_2	0.05 μF
R_3	1 MΩ	C_3	0.05 μF
R_4	2 KΩ	C_4	0.1 μF
R_5	2 KΩ	C_5	100 μF
R_6	20 KΩ	C_6	0.1 μF
R_7	4 KΩ	C_7	100 μF
R_8	300 Ω	C_8	2 μF
R_9	100 KΩ	C_9	0.1 μF
R_{10}	50 KΩ	C_{10}	100 μF
R_{11}	1 KΩ	C_{11}	0.02 μF
R_{12}	1 KΩ	C_{12}	100 μF
R_{13}	1 KΩ	V_1	1/2 6SL7
R_{14}	130 KΩ	V_2	1/2 6SL7
R_{15}	1 MΩ	V_3	1/2 6SL7
R_{16}	100 KΩ	V_4	1/2 6SL7
VR_1	50 KΩ	V_5	6BD6
VR_2	1 MΩ	V_6	1/2 6SN7
VR_3	500 KΩ	V_7	1/2 6SN7
VR_4	500 KΩ	V_8	6J5
VR_5	500 KΩ		

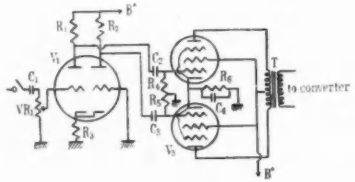

Fig. 6

R_1	100 KΩ	C_1	0.1 μF
R_2	100 KΩ	C_2	0.1 μF
R_3	1 KΩ	C_3	0.1 μF
R_4	250 KΩ	C_4	100 μF
R_5	250 KΩ	V_1	6SL7
R_6	210 Ω	V_2	UZ42
VR_1	500 KΩ	V_3	UZ42

the temperature coefficient is about −5.5 percent at 25°C and thus it corresponds to about $1/2\times10^{-4}$ degree.

Very little amounts of polarization in the thermister, probably due to the ions present, were observed. But the experiments were not affected, for the measurements were carried out after the polarization had been saturated. Thermoelectromotive force in the bridge circuit was cancelled by adjusting a variable resistor V in Fig. 3.

Methods of Operation. After setting the calorimeter in the thermostat regulated at $25\pm1\times10^{-4}$°C, temperature of the calorimeter was adjusted

9) N.A. Schuster, *Rev. Sci. Inst.*, **22**, 254 (1951).

almost equal to that of the thermostat by heating. It was then left for three to five hours in order to establish the thermal equilibrium.

The resistance reading was started after the calorimeter had reached thermal equilibrium. After mixing the solution and the solvent, the resistance reading was taken at an interval of one minute for about twenty minutes and a cooling curve was constructed. The heat change was always complete in two or three minutes. The heat capacity was determined for each run by introducing a certain amount of electrical energy which produces approximately equal resistance change to that in the mixing. The mixed solution was stirred manually by moving the inner bulb up and down from 10 times to 30 times according to the viscousness of the mixed solution until no inhomogeneity of the solution was observed. A stirring correction for the mixing was obtained by stirring the already mixed solution by the same standard technique as that employed in the mixing.

During the stirring, heat was developed and was quite reproducible in the cases of toluene and ethylbenzene, both having fairly low vapor pressure at 25°C. In the case of chloroform, however, reproducibility was not so satisfactory. This may be as-cribed to the fact the latter solvent has a fairly high vapor pressure at 25°C, and evaporates during the stirring and its amount is irregular because of the manual operation.

Materials.—A sample of Polystyrene* was prepared by polymerizing the monomer in carbon tetrachloride. This sample was purified by dissolving in benzene and precipitating with methanol. The same procedure was repeated twice and dried for about a week under the pressure of 1 mmHg.

The solvents used were purified according to the method described in the literature and finally distilled. Toluene, ethylbenzene** and chloroform used were fractions having boiling point 110.8–111.2°C, 135.5–136.0°C and 61.1–61.2°C respectively.

Results and Discussion

The heat of dilution was measured by adding 5 or 10 cc. of solvent successively to the solution of a definite concentration. The results obtained are shown in Table I.

Assuming that the heat of mixing is represented by the van Laar form, the heat of mixing H_m of solvent of volume V_0 and polystyrene of volume V_r can be represented as:

$$H_m = \alpha V_0 V_r/(V_0+V_r), \tag{1}$$

where α is a constant describing the interaction between solute and solvent. Accordingly, when the solvent of volume dV_0 is added to this solution, its heat of dilution is given by:

$$dH_d = (\partial H_m/\partial V_0)_p dV_0 = [\alpha V_r^2/(V_0+V_r)^2]\cdot dV_0. \tag{2}$$

Thus, the integral heat of dilution ΔH_0 obtained when the solvent of the volume ΔV_0 is added to this solution is given by:

$$\Delta H_0 = \int dH_d = \int_{V_0}^{V_0+\Delta V_0} [\alpha V_r^2/(V_0+V_r)^2] dV_0. \tag{3}$$

Assuming that α is constant within a small

TABLE I

HEAT OF DILUTION OF POLYMER SOLUTION

	Before dilution V cc.	v_r	After dilution V' cc.	v_r'	Heat evolved cal.	$-\alpha_d$	$-\alpha_{av}$	$-\mu$
1. Polystyrene-toluene system.								
1	4.70	0.189	9.70	0.092	0.099	1.14		
	9.70	0.092	14.70	0.060	0.035	1.26	1.37	0.24
	14.70	0.660	19.70	0.045	0.025	1.82		
2	4.70	0.170	9.70	0.083	0.106	1.51		
	9.70	0.083	14.70	0.055	0.037	1.64	1.51	0.27
	14.70	0.055	19.70	0.041	0.014	1.29		
3	9.70	0.083	14.70	0.055	0.037	1.64	1.51	0.27
	14.70	0.055	19.70	0.041	0.016	1.41		
2. Polystyrene-chloroform system.								
1	4.75	0.275	9.75	0.134	0.234	1.28		
	9.75	0.134	14.75	0.088	0.122	1.29	1.36	0.17
	14.75	0.088	19.75	0.066	0.046	1.58		
2	4.70	0.171	9.70	0.083	0.081	1.11	1.13	0.14
	9.70	0.083	14.70	0.055	0.028	1.25		
3. Polystyrene-ethylbenzene system.								
	4.75	0.194	9.75	0.081	0.002	0.02	0.00	0.00
	9.75	0.081	14.75	0.053	−0.002	−0.07		

* We are indebted to Prof. T. Matsumoto of the Faculty of Technology of our University for this sample.

** We wish to thanks Dr. H. Yoshida of the Government Industrial Research Institute, Osaka, for supplying purified ethylbenzene.

concentration range (of course it is generally concentration dependent), we can express (3) as follows:

$$\Delta H_0 = -\alpha[V_r^2/(V_0+\Delta V_0+V_r) - V_r^2/(V_0+V_r)] \quad (4)$$

If we introduce the quantities V, V', v_r and v_r' defined as:

$V_0+V_r=V$ (Total volume of solution before dilution),
$V_0+\Delta V_0+V_r=V'$ (Total volume of solution after dilution),
$v_r=V_r/(V_0+V_r)$ (Volume fraction of polymer before dilution),
$v_r'=V_r/(V_0+\Delta V_0+V_r)$ (Volume fraction of polymer after dilution),
the above expression can be written as follows:

$$\Delta H_0 = \alpha(Vv_r^2 - V'v_r'^2). \quad (5)$$

The amount of polystyrene in the solution is the same before and after the dilution. Then (5) can be written as:

$$\Delta H_0 = \alpha V_r(v_r - v_r'). \quad (6)$$

Plotting ΔH_0 obtained from the experiment as ordinate and v_r as abscissa for each of three systems, we obtain a straight line in each case in the concentration range from 0.2 to 0.05 volume fractions. As an example, H_0-v_r diagram of the polystyrene-toluene system is shown in Fig. 7.

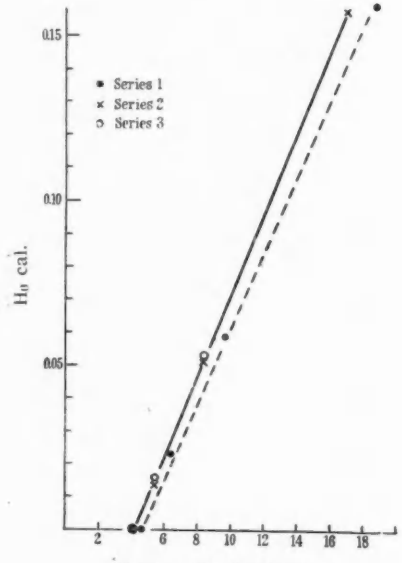

Fig. 7. Polystyrene—Toluene Solution.

α can be obtained from the tangent of the straight line in the diagram and its value for each system is given in Table I as $\alpha_{av.}$ Using (5), α at each concentration can be evaluated and the values thus obtained are represented as α_a. From these α values, μ can be derived by the equation, $\mu=\bar{V}\alpha/RT$, where $\bar{V}$ is the partial molal volume of the solvent, and shown in Table I.

For the sake of comparison with these data, the heat of mixing and the heat of dilution of ethylbenzene, which may be regarded as a monomer unit of polystyrene, with toluene and chloroform were also measured and the results are shown in Table II. From these

TABLE II

HEAT OF DILUTION OF MONOMER-UNIT (ETHYLBENZENE) SOLUTION

1. Ethylbenzene-toluene system.

	Before dilution V cc.	v_r	After dilution V' cc.	v_r'	Heat evolved	$-\alpha_m$	$-\alpha_a$
1	5	1.000	10	0.500	0.206	0.08	
	10	0.500	15	0.333	0.098	0.09	0.20
	15	0.333	20	0.250	0.070	0.10	0.17
2	3	1.000	6	0.500	0.124	0.08	
	6	0.500	9	0.333	0.074	0.10	0.15

2. Ethylbenzene-chloroform system.

	2	1.000	4	0.500	5.619	5.62	
	4	0.500	6	0.333	2.030	5.74	6.09
	6	0.333	8	0.250	1.135	5.86	6.81
	8	0.250	10	0.200	0.653	5.90	6.53
	10	0.200	12	0.167	0.243	5.81	3.65
	12	0.167	17	0.116	0.343	5.68	3.47

data α values were calculated by the same procedure as in the polystyrene under the assumption that the equations (1) and (5) can also be applied. These values are shown in Table II as α_m and α_a respectively.

It is interesting that the interaction parameters between polymer and solvents have the same signs as those between monomer unit of polymer (ethylbenzene) and that the polymer-monomer unit system is athermal. That the polymermonomer unit system is athermal was confirmed by Meares[7] in the polyvinylacetateethylacetate system.

It is expected that α or μ for the polymer-solvent system is smaller in magnitude than that for the monomer unit-solvent system owing to the self-contact between polymer segments. But for the polystyrene-toluene system the reverse was observed. From this fact it is expected that there are some anomalous phenomena which might be explained by measuring the volume change or the changes of other physical properties on mixing for this system.

TABLE III

COMPARISON WITH THE DATA OBTAINED BY VARIOUS METHOD

1. Polystyrene-toluene system.

Observer	Method	$-\mu$	Temperature °C	Volume fraction	D.P.
Tompa[8]	a	0.10–0.17	25	0.25–0.40	17–30
Bawn et al[3]	b	0–0.01	25–55	0.003–0.009	$(1.5–3)\times10^3$
Doty et al[4]	b	0.17–0.04	27–69	0.01–0.08	540
Schulz[10]	b	0.09–0.05	15–40	0.01–0.03	90
Schulz et al[11]	b	0.03–0.04	20–42	0.03	$(2.3–5.8)\times10^3$
This experiment	a	0.24–0.27	25	0.04–0.19	275

2. Polystyrene-chloroform system.

Bawn et al[3]	b	0	25–55	0.2–0.6	$(1.5–3)\times10^3$
Schulz et al[11]	b	0.02	20–42	0.03	$(2.3–5.8)\times10^3$
This experiment	a	0.14–0.17	25	0.05–0.27	275

Method a: Direct measurement.
b: From the temperature dependence of osmotic pressure or vapor pressure.

Our results are compared with the previous data obtained by various methods, and shown in Table III. For the chloroform-polystyrene system, it is found that the μ value is negative and large. This is consistent with the fact that chloroform is a good solvent for polystyrene. That the μ value obtained by Bawn and Wajid[5] from the temperature dependence of vapor pressure was zero, is in marked contrast to our result.

A direct measurement of heat of dilution for the toluene-polystyrene system was carried out by Tompa[8]. His value was the same in sign but different in magnitude. The degree of polymerization of the sample used by him was from 17 to 30, but our sample had a degree of polymerization of about 275. From the μ values obtained for various samples of different polymerization degree, ($\mu=-0.27$ for D.P.$=275$, -0.17 for 17 to 30, -0.03 for 1) it seems that an apparent correlation exists between the μ value and the polymerization degree. But for a definite conclusion, further investigation will be needed.

Summary

A calorimeter equipped with a thermister capable of measuring the temperature change down to 0.5×10^{-4}°C was constructed. By this apparatus the heats of dilution of three polystyrene solutions were measured and the values of interaction parameters were derived. The μ values for toluene solution and chloroform solution were both negative and large, but that for ethylbenzene solution was zero.

In order to compare with the polymer solution, the heat of mixing of ethylbenzene, which may be regarded as the monomer-unit of polystyrene, with same solvents were also measured and it was found that the interaction parameters of polymer solutions have the same signs as that of the corresponding monomer-unit solutions.

We should like to express our gratitude to Professor Y. Morino of Tokyo University and Professor A. Kotera of Tokyo University of Education for there kind encouragement and discussions throughout the work. We are also greateful to Mr. K. Suzuki for his helpful discussions.

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Studies on the Supplementary Reduction in Oscillographic Polarography

By Hideo IMAI

(Received August 8, 1955)

A supplementary kink was found in the oscillographic potential-time curve of the metal ion such as Cd^{++} which exists in a neutral solution containing the dissolved oxygen. Vogel[1] was the first who reported the phenomenon, which was more recently assigned to a sudden decomposition of a metal hydroxide by Behr and Chodkowski[2].

In this paper are presented the results of detailed studies of the phenomenon by means of a current-potential oscillographic polarograph and a proposal of a new mechanism of the effect.

Experimental

The technique of the oscillographic current-potential curve introduced by Ševčik[3] was used with some modifications[4]. The arrangement is illustrated in Fig. 1. The cell used was a H-cell with double partitions made with sintered glass disks, and a supporting electrolyte solution was instilled in a compartment between a test solution and a saturated calomel electrode. Thus, the contamination of a test solution by chloride ion was avoided.

To prepare all test solutions reagent grade chemicals were recrystallized twice from their aqueous solutions.

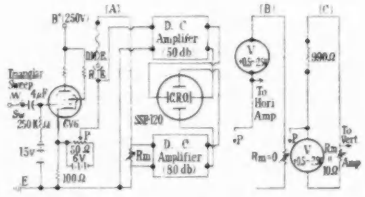

Fig. 1. Schematic diagram of measuring apparatus. (A) polarographic circuit. (B) and (C) calibrating circuit for horizontal and vertical deflection, respectively.

In the solution of Pb^{++}, Zn^{++}, Bi^{+++}, Al^{+++}, or Fe^{+++} no reproducible current was observed, owing to the irregular fluctuation of the lifetime of the D. M. E. (Sometimes it amounts to a variation as large as 10% of the mean life time.). Accordingly, Cd^{++} in N KCl was used for the quantitative measurements. The possible experimental error in measuring the polarographic current amounts to $\pm 3\%$[5].

Results

1. Influence of the Dissolved Oxygen.— In an ordinary polarography the reduction of the metal ion such as Cd^{++} in a neutral

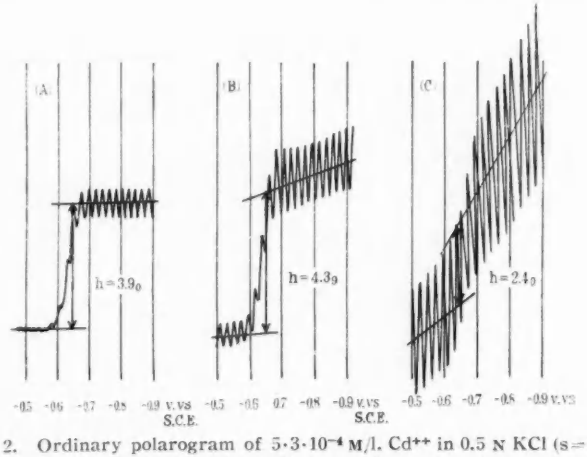

Fig. 2. Ordinary polarogram of $5 \cdot 3 \cdot 10^{-4}$ M/l. Cd^{++} in 0.5 N KCl (s=1/20, 24.6° C). (A) deaerated soln., (B) test soln. contg. atm. oxygen, (C) test soln. contg. conc. oxygen.

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medium gives the current-potential curve irreversible to some degree. The limiting current increases as the concentration of oxygen increases. However, the presence of oxygen in its high concentration results in the reduction of the diffusion controlled current. The typical polarograms of these cases are illustrated in Fig. 2.

In the oscillographic current-potential polarogram a reduction peak and a reoxidation peak can be observed in the cathodic and anodic branches, respectively. Dissolved oxygen being present in a neutral Cd^{++} solution, the normal reduction peak, i.e. the reduction peak of an aquo cadmium ion, is lowered and it accompanies a supplementary reduction peak, while no remarkable change is observed in the anodic branch as is illustrated in Fig. 3.

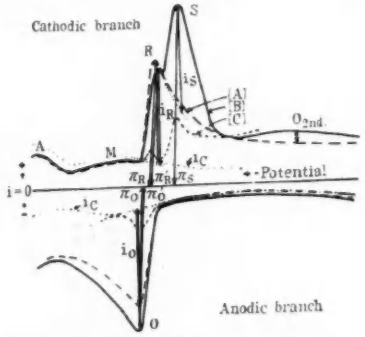

Fig. 3. Oscillographic polarogram of 1.10^{-3} M/l Cd^{++} in N KCl (20 c.p.s., v= 50 v/s): Full curve, interrupted curve and dotted curve correspond to (A), (B) and (C) of Fig. 2, respectively.

This effect can be observed not only in a multi-sweep method, but also in a single sweep method. As the concentration of the dissolved oxygen increases, at first the normal reduction peak lowers and, on the contrary, the supplementary reduction peak increases attaining a maximum value, then all peaks begin to decrease simultaneously, being extinguished ultimately.

Since, the shift of the initial sweep voltage toward more positive potential elongates the duration of the first oxygen reduction, the influence of the dissolved oxygen can be best realized by changing the initial sweep voltage.

The plot of the relation between the peak height and the initial sweep voltage is illustrated in Fig. 4. When the initial sweep voltage is shifted toward more positive potentials, at first the supplementary reduction peak remarkably increases and it amounts to a limiting value at −0.05 volts vs. S. C. E., which coincides with the half wave patential of the first oxygen reduction in N KCl*.

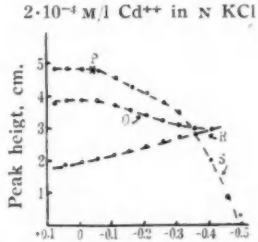

Fig. 4. Variation of the peak height with the initial sweep voltage. 20 c.p.s., v= 50 v/s, $2.0.10^{-4}$ M/l Cd^{++}.

It must be recalled here that in the oscillographic technique the applied voltage sweeps during a single lifetime of the D.M.E., therefore, the electrode suffers from the hysteresis of a prior reduction (namely, the first reduction of the dissolved oxygen in this case.). Since the supplementary reduction does not affect the second oxygen reduction, it may be assumed that the hydroxide ion formed in the course of the first oxygen reduction plays a role in the supplementary reduction.

2. Influence of the Concentration of a Metal Ion.—The plot of the relation between the wave height and the concentration of Cd^{++} is illustrated in Fig. 5, where the full curve and the interrupted curve represent the plot in the cases of the deäerated and the undeäerated solutions, respectively. In the former case a good linearity is obtained by the ordinary polarograph concurring with Ilkovič's equation, while in the latter case the linearity deviates slightly. Likewise, in the deäerated solution a linear plot is obtained by the oscillographic technique, while in the undeäerated solution the supplementary reduction peak steeply increases at first as the Cd^{++} concentration increases, and it amounts to a limiting value at a certain Cd^{++} concentration (i.e., about 0.5 mM/l, which is

* Behr and Chodkowski[2] coined the term "latent limiting current" for the first oxygen reduction in an potential-time oscillographic method. The present author has assigned the effect to its irreversible process and also to the fact that the cathodic current has probably been likely misjudged for a large charging current. The peak current of the dissolved oxygen was observed in the surfaceinactive supporting electrolyte such as nitrate, perchlorate or sulfate, while it was not observed in the solution containing halogen ion. The electrode reaction proceeds as follows:

1st reduction: $O_2+2H_2O+2e=H_2O_2+2OH^-$

2nd reduction: $H_2O_2+2e=2OH^-$

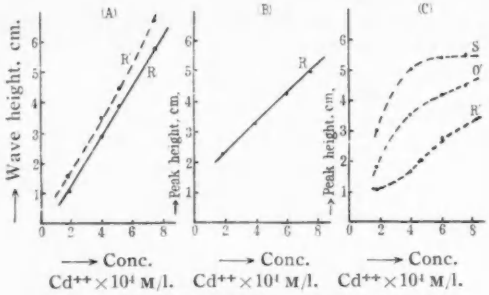

Fig. 5. Variation of the wave height with the conc. of Cd^{++}: (A); ordinary polarograph (s=1/20), (B) and (C): oscillographic polarograph (20 c.p.s., v=36 v/s): full curve; deäerated soln., interrupted curve; test soln. contg. atm. oxygen.

greater than the equivalent concentration of the dissolved oxygen (0.3_3 mM/l.)).

These results seem to indicate that the simultaneous reduction of Cd^{++} and oxygen does not affect the diffusion controlled current of Cd^{++} as the case is an ordinary polarograph, but in the oscillographic polarograph the hydroxide ion formed in the course of the first oxygen reduction changes an aquo Cd^{++} into cadmium hydroxide which pertains to the increment of the supplementary reduction.

3. Variation of the Peak Height with the Rate of Potential Change.—The peak height of Cd^{++} is linearly proportional to the square root of the rate of potential change in the range of 20–60 volts per second. The supplementary reduction behaves similarly, however, the gradient of the plot is about two and a half times greater than that of the normal reduction as is illustrated in Fig. 6. This effect is assigned to the fact that not only the reduction of Cd^{++} but also that of the dissolved oxygen increase with the increase of the rate of potential change,

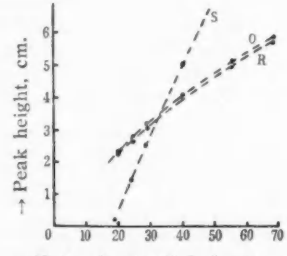

Fig. 6. Variation of the peak height with the rate of potential change, v. (20 c.p.s., $V_i=-0.30$ v. vs. S.C.E., $1\cdot10^{-3}$ M/l. Cd^{++}).

therefore, the increase of the supplementary reduction results from the conjoined effect of two reducible species, i.e. Cd^{++} and oxygen.

4. Influence of the Concentration of Hydrogen Ion.—The supplementary reduction can be observed in the neutral solution of bromide, chloride, rhodanate, nitrate or sulfate. However, there is a limit in an acidic or in an alkaline solution. The influence of pH on the supplementary reduction was persued in non-buffered media, and the results are illustrated in Fig. 7.

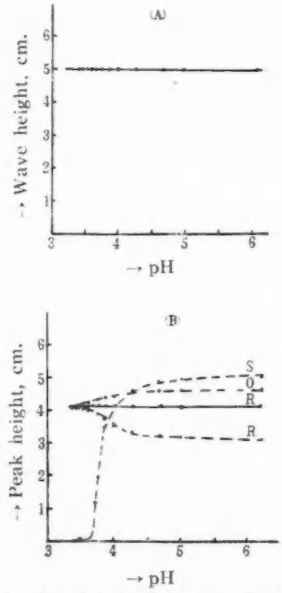

Fig. 7. Variation of the wave height with pH: (A) ordinary polarograph (s=1/20), (B) oscillographicp olarograph: full curve; deäerated soln., interrupted curve; test soln. contg. atm. oxygen.

In the ordinary polarography pH does not affect the diffusion controlled current of Cd^{++}. Also in the oscillographic work the normal reduction in the case of the deäerated solution is independent of pH. On the contrary, the effect is remarkable in the undeäerated solution. When pH of the test solution is less than 3.53 the supplementary reduction was not observed. In the pH range from 3.53 to 3.67 the supplementary reduction gradually increases as the D. M. E. drops repeatedly. Hence, the peak height recorded during the first single drop was taken into account. In Fig. 7 the supplementary reduction increases as pH increases, while the normal reduction varies vice versa. The supplementary reduction was not observed in

the buffered solution containing N acetic acid and N sodium acetate.

As a result, it may be assumed that the variation of the solubility of a metal hydroxide in an acidic solution results in the variation of the supplementary reduction. This effect corresponds to the fact that the metal ion which gives rise to the supplementary reduction in a neutral medium is confined to its ability to form the sparingly soluble hydroxide. Only Cd^{++}, Pb^{++}, Zn^{++}, Bi^{+++}, Fe^{+++} or Al^{+++} was found to give the supplementary reduction.

From these results it is evident that the supplementary reduction results from the sparingly soluble metal hydroxide. It can not be elucidated, however, that not only the normal reduction but also the supplementary reduction decrease by the presence of oxygen in its high concentration. The following experiment was pursued to clarify this point.

5. Variation of the Peak Height with the Mercury Head.—In an ordirnary polarography, the variation of the limiting current is linearly proportional to the square root of the mercury head as is illustrated in Fig. 8 Aa. However, in an oscillographic polarograph the peak height is practically independent of the mercury head (Fig. 8 Ba). These relations deviate in the case of the undeäerated solution (Figs. 8 Ab, 8 Bb), especially by the presence of oxygen in its high concentration (Figs. 8 Ac, 8 Bc).

The presence of oxygen in its high concentration results in the depletion of a reducible metal ion by the formation of a metal hydroxide at the electrode surface.

When the mercury head is raised, the rate of the drop growth of the D. M. E. increases in proportion to the mercury head, and accordingly, the expanding electrode surface can encounter the reducible metal ion which locates a little apart from the electrode surface.

From the fact that not only the normal reduction but also the supplementary reduction increase as the mercury head is raised, it is reasoned that the supplementary reduction is originated from an intermediate, i. e. a colloidal metal hydroxide, between an aquo metal ion and a metal hydroxide.

6. The Microscopic Observation of the D. M. E.—When the supplementary reduction arises, a smoky cloud is observed microscopically as the case is Pb^{++} or Fe^{+++}. The smoky cloud is formed at the vicinity of the

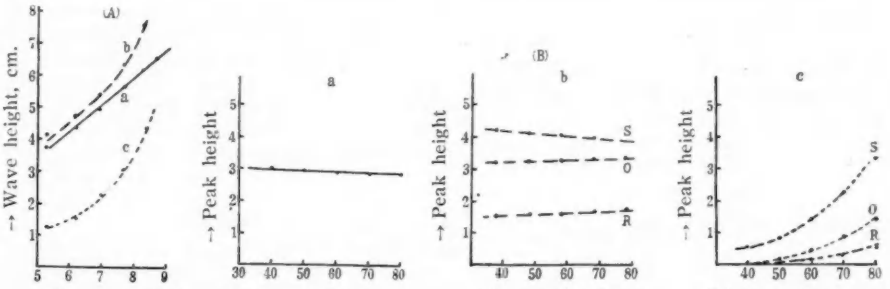

Fig. 8. Variation of the wave height with the mercury head: ($5.3 \cdot 10^{-4}$ M/l Cd^{++} in 0.5 N KCl), (A) ordinary polarograph, (B) oscillographic polarograph: full curve; deäerated soln., interrupted curve; test soln. contg. atm. oxygen, dotted curve; test soln. contg. conc. oxygen.

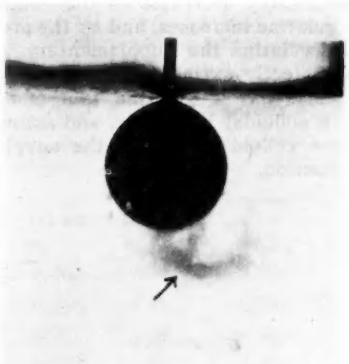

Fig. 9. Photomicrograph of metal hydroxide colloids repulsed from the surface of the D.M.E.

D. M. E. at an early stage of the lifetime, and some time after it is suddenly repulsed from the electrode surface prior to the drop of the D. M. E. The photomicrograph is illustrated in Fig. 9.

It may be assumed that a colloidal metal hydroxide is formed by the reaction of a metal ion with a hydroxide ion, and being deprived of the stabilizing ion as the result of the supplementary reduction, the metal hydroxide is repulsed by the negatively charged electrode. This assumption will be supported by the following experiment.

7. Influence of the Surface Active Reagent.—The variation of the peak height with the concentration of gelatine is illustrated in Table I.

Both Triton X 100 and dodecyl-trimethyl ammonium chloride give the same results as that of gelatine.

Conclusion

From the above mentioned results the mechanism of the supplementary reduction can be given as follows.

At first the dissolved oxygen is reduced at the vicinity of the electrode surface to form a colloidal metal hydroxide with an aquo metal ion. When the cathodically produced hydroxide ion is not as much as the equivalent concentration of the metal ion, the excess metal ion is adsorbed around the colloidal metal hydroxide as the inner ion (i. e. the potential determining ion) of the colloid.

TABLE I

VARIATION OF THE WAVE HEIGHT WITH THE GELATINE CONCENTRATION

A. Ordinary Polarograph: sensibility=1/20						
Gelatine conc., %		0	0.005	0.01	0.05	0.1
Wave height of Cd^{++} in deaerated soln., cm.		5.85	5.85	5.85	5.65	5.50
In the test soln. containing oxygen, cm.		6.12	5.92	5.92	5.78	5.78
B. Oscillographic Polarograph: v=50 v/s, 20 c.p.s.						
Gelatine conc., %		0	0.005	0.01	0.05	0.1
Peak ht. of Cd^{++} in deaerated soln., cm.	R	3.85	3.80	3.77	2.40	2.40
	O	3.87	3.90	3.90	3.80	2.80
In the test soln. contg. oxygen, cm.	R	3.11	3.75	3.80	3.21	2.99
	S	4.04	2.75	2.70	0	0
	O	4.39	3.92	3.74	2.87	2.62

In Table I, A the reduction of Cd^{++} is not hindered by the presence of 0.01% gelatine in the case of the deaerated solution, however, in the undeaerated solution the reduction is hindered even by the presence of 0.005% gelatine. In Table I, B the normal reduction is retarded only a little by the presence of gelatine. However, the supplementary reduction remarkably decreases as the concentration of gelatine increases, and by the presence of 0.05% gelatine the supplementary reduction is perfectly extinguished.

It seems that a gelatine film is formed around a colloidal hydroxide, and acting as a protective colloid it retards the supplementary reduction. This inner ion will give rise to the supplementary reduction. The potential required for the reduction of the inner ion will be greater than the aquo metal ion on account of its Coulombic attraction to the metal hydroxide. Thus, the supplementary reduction is observed at the more negative potential than the normal reduction.

The author wishes to express his hearty gratitude to Prof. Mutsuaki Shinagawa for his valuable advice and encouragement. Also the author thanks Mr. Shōkichi Chaki who assisted in a part of this experiment.

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Studies on Electrocapillarity with Respect to the Supplementary Reduction in Oscillographic Polarography

By Hideo IMAI

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The mechanism of a supplementary reduction has been proposed in a previous report[1], where the supplementary reduction was assigned to the reduction of the inner metal ion (the potential determining ion which establishes the electrical double layer of a colloidal metal hydroxide with the counter ion (anion)). Hence, the difference between the peak potential of the normal reduction (i.e. the reduction of an aquo metal ion) and that of the supplementary reduction may be the measure of Coulombic attraction between the inner ion and the colloidal metal hydroxide. In this paper are presented the estimation of the Coulombic attraction in various supporting electrolytes and some related phenomena.

Experimental

The multi-sweep oscillographic technique of a current potential curve was employed[1]. The rate of potential change, 70 v./s. (20 c.p.s.), was used throughout the measurments. Waves were recorded during the lifetime of a single drop, but for the sake of clarity, only the pattern corresponding to the maximum size of the mercury drop is shown in Figs. 1-4. In general it is observed that the cathodic peak potential is shifted toward more negative values as the drop grows. This shift is caused by an increase in the ohmic drop in the cell and the measuring circuit. Likewise, the anodic peak potential is shifted toward more positive potentials as the drop grows. The shift in the peak potential is indicated in Figs. 1-3 by a straight line. In order to obtain correct peak-potentials it suffices to extrapolate the potential to zero current as is indicated in Figs. 1-3. The possible error in measuring the peak potential amounts to ± 0.005 volt.

The test solution contains about 1 mM/l. Cd^{++}, Pb^{++} or Zn^{++} in N KI, KBr, KCl, KNO_3, $NaNO_3$, Na_2SO_4 or sat. K_2SO_4 and about 0.37 mM/l. oxygen equilibrated with atmospheric oxygen at 25°C. In the preparation of these solutions, reagent grade chemicals were recrystallized twice from their aqueous solutions.

The temperature was 25 ± 0.1°C.

Results

The current-potential curves are illustrated in Figs. 1-3, where full curves and dotted curves denote those of the deäerated solutions and of the undeaerated solutions, respectively. The charging current, i_c, in each solution is also appended.

From these polarograms, peak potentials were estimated by the method described in the preceding section, and are illustrated in Tables I-III. It was confirmed that the peak potential of a metal ion in the presence of the dissolved oxygen approximately coincides with that of a metal ion in the deäerated solution within the experimental error.

TABLE I

$1 \cdot 10^{-3}$ M/l. Cd^{++} IN N KnX

X^{n-}	π_R	π_S	π_0	$(\pi_R+\pi_0)/2$	$\pi_R-\pi_S$
I^-	-0.75_5	—	-0.73_0	-0.74_3	—
Br^-	-0.68_3	-0.81_0	-0.63_5	-0.65_8	0.13_0
Cl^-	-0.67_0	-0.80_5	-0.61_0	-0.64_0	0.13_5
OS_4^{--}	-0.63_0	-0.79_0	-0.56_5	-0.59_7	0.16_0
NO_3^-	-0.62_0	-0.79_0	-0.56_0	-0.59_0	0.17_0

TABLE II

$1 \cdot 10^{-3}$ M/l. Pb^{++} IN N KnX. [( ); ILL-DEFINED DATA]

X^{n-}	π_{R1}	π_{R2}	π_{S1}	π_{S2}	π_{01}	π_{02}	$(\pi_{R2}+\pi_{02})/2$	$\pi_{R2}-\pi_{S1}$
I^-	-0.59_5	-0.67_5	—	—	(-0.80_0)	-0.59_0	-0.63_3	—
Br^-	-0.47_5	-0.52_5	-0.60_8	(-1.00_0)	(-0.66^0)	-0.48_0	-0.50_3	R1 : 0.13_7 R2 : 0.08_3
Cl^-	—	-0.48_0	-0.61_0	(-1.04_0)	(-0.51_0)	-0.40_5	-0.44_3	0.13_0
NO_3^-	—	-0.45_0	-0.62_7	(-1.05_0)	(-0.45_7)	-0.35_0	-0.40_0	0.17_7
OH^-	—	-0.80_0	—	—	—	-0.70_0	-0.75_0	—

1) H. Imai, This Bulletin, 29, 276 (1956).

TABLE III

$1 \cdot 10^{-3}$ M/l. Zn^{++} IN N KnX. [( ); ILL-DEFINED DATA]

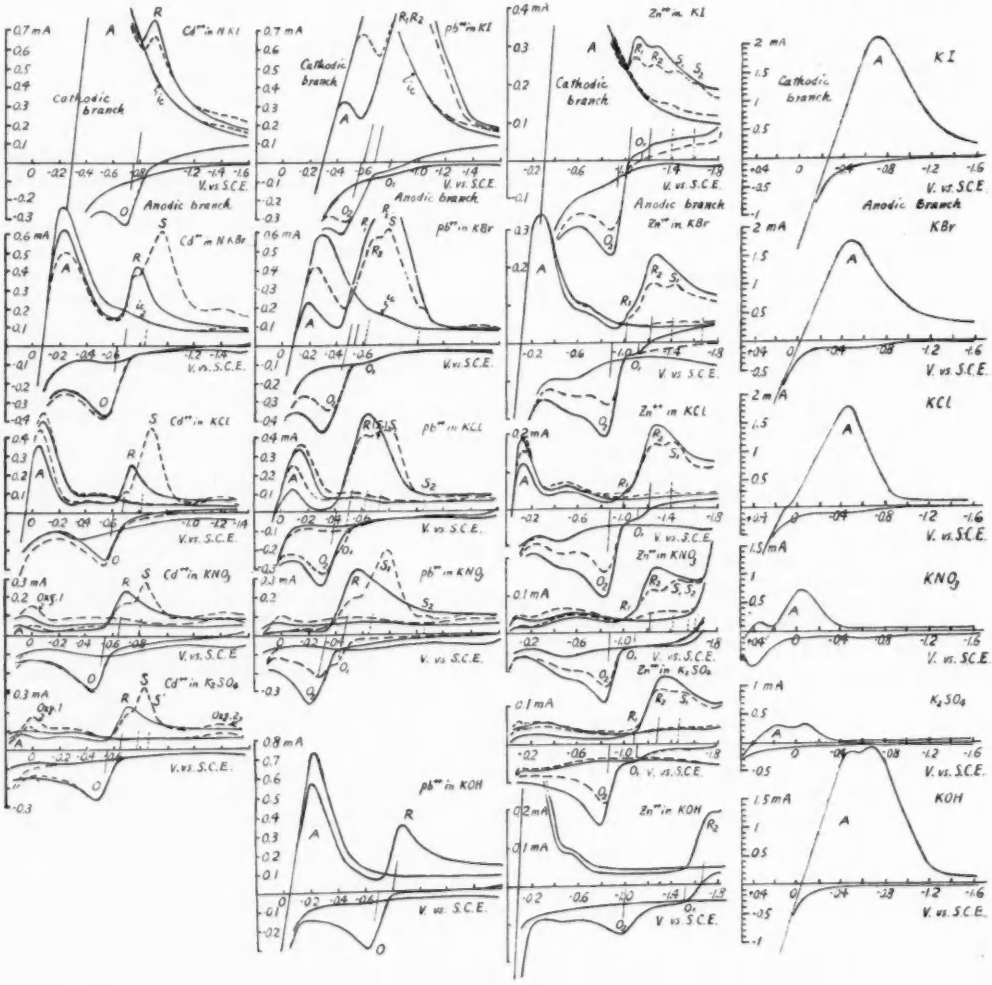
X^{n-}	π_{R1}	π_{R2}	π_{S1}	π_{S2}	π_{01}	π_{02}	$(\pi_{R2}+\pi_{02})/_2$	$\pi_{R22}-\pi_{S1}$
I^-	(-1.01_8)	-1.20_0	-1.38_2	(-1.59_3)	(-1.12_5)	-0.93_8	-1.06_9	-0.18_2
Br^-	(-1.00_0)	-1.20_0	-1.39_0	—	(-1.12_0)	-0.90_2	-1.05_1	-0.19_0
Cl^-	(-0.90_0)	-1.20_0	-1.39_5	—	(-1.11_8)	-0.88_0	-1.04_0	-0.19_5
SO_4^{--}	(-1.10_0)	-1.22_0	-1.42_0	(-1.56_0)	(-1.11_0)	-0.88_0	-1.05_0	-0.20_0
NO_3^-	(-1.10_0)	-1.20_2	-1.40_5	(-1.55_0)	$(-1.11'_0)$	-0.87_5	-1.03_8	-0.20_3
OH^-	—	-1.71_0	—	—	-1.50_0	-1.00_5	-1.36_7	—

Fig. 1. Oscillographic polarogram of $1 \cdot 10^{-3}$ M/l. Cd^{++} in N KnX (X=negative ion).

Fig. 2. Oscillographic polarogram of $1 \cdot 10^{-3}$ M/l. Pb^{++} in N KnX.

Fig. 3. Oscillographic polarogram of $1 \cdot 10^{-3}$ M/l. Zn^{++} in N KnX.

Fig. 4. Oscillographic polarogram of N KnX (X=negative constituent of supporting electrolyte.).



In the current-potential oscillogram of Cd^{++} in N KBr or in N KCl the second supplementary reduction is perceptible by a judicious choice of the initial sweep voltage. Also in the oscillogram of Cd^{++} in K_2SO_4 the supplementary reduction consists of double peaks regardless of any control of the applied sweep. All these auxiliary peaks are ill-defined and are omitted.

In the solutions containing Zn^{++}, the normal reduction waves consist of two peaks in the cathodic branch and in the anodic branch, respectively. This characteristic shape has been discussed by Delahay[2]. However, the remarkable consecutive peaks shown in the case of Zn^{++} in N KBr or KI can not be elucidated by Delahay's concept. The problem remains for the future[3].

The second supplementary reduction, S_2, observed in the case of Pb^{++} or Zn^{++} is that of the hydroxide complex such as $HPbO_2^-$, $HZnO_2^-$. These hydroxide complexes result from their amphoteric nature.

Among these complicated results, the following features hold in common:

(1) Both the peak potential of the normal cathodic process, π_R, and that of the anodic process, π_0, are shifted toward more negative potentials in the solutions of NO_3^-, SO_4^{--}, Cl^-, Br^-, I^- in the order given. The mean potential, $(\pi_R+\pi_0)/2$, behaves likewise.

(2) The values of $\pi_R-\pi_S$ (π_S; the peak potential of the supplementary reduction) increase in the solutions of I^-, Br^-, Cl^-, (SO_4^{--}, NO_3^-) in the order given.

These common features seem to correlate intimately with the electrocapillary behaviors of anions as shown in the following.

The current-potential oscillograms of deaerated supporting electrolytes are shown in Fig. 4.

In every solution an enormously large charging current passes through the cell in the cathodic branch. Every charging current attains a maximum at an appreciably positive or a less negative potential (The potential of the maximum charging current is always positive with respect to the potential referred to the electrocapillary maximum.), then decreases gradually as the applied potential sweeps toward more negative potentials. It is interesting that such a large charging current is not observable in the anodic branch. Moreover, such a current can not be observed by an ordinary polarograph. This irreversible current can be assigned to the variation of a differential capacity as is shown in the following.

The charging current consists of two components, one is the charging current, i_{c_1}, due to the increase in capacity of the electrical double layer and another is the charging current, i_{c_2}, due to the differential capacity. Since the complete current-potential curve is recorded in a small fraction of the drop life, i.e. 1/20 seconds in this experiment, i_{c_1} is very small.

The charging current, i_{c_2}, is equal to the rate of flow of charge due to the variation of the differential opacity, c, i.e.

$$i_{c_2}=\frac{dQ}{dt}=c\frac{dE}{dt} \tag{1}$$

Under the condition of the experiment where a linearly increasing and decreasing potential sweep is applied to the D.M.E. the rate of potential change with respect to time, t, is equal to a constant, v.[4] Hence,

$$\frac{dE}{dt}=v \qquad \therefore \quad i_{c_2}=c\cdot v \tag{2}$$

The linear relation between i_{c_2} and v has been verified experimentally by the present author[5]. Since v is as large as 70 v./s. in this experiment, i_{c_2} is enormously large and i_{c_1} is negligible.

Integration of equation (1) leads to an equation for the charge flowed (Q):

$$Q=\int_{E_1}^{E_2} c\ dE+k \tag{3}$$

Substituting Eq. 2 into Eq. 3, one has:

$$Q=\frac{1}{v}\int_{E_1}^{E_2} i_{c_2}dE+k \tag{4}$$

where E_1 is the potential of the D.M.E. and E_2 is that of an electrocapillary maximum.

Supposing the surface area of the D.M.E. is kept constant, the area surrounded by the charging current curve means the surface charge density.

The surface area of the D.M.E. is proportional to $m^{2/3}\ t^{2/3}$ (m; the flow rate of mercury, t; the lifetime of the D.M.E.). In this experiment m is constant and t decreases in the solutions of (NO_3^-, SO_4^{--}), Cl^-, Br^-, I^- in the order given. Hence, the surface area of the D.M.E. under a given applied sweep increases in the solutions of I^-, Br^-, Cl^-, (SO_4^{--}, NO_3^-) in the order given, while from Fig. 4 Q increases vice versa. Hence, the surface charge density at a given applied potential decreases in the solutions of I^-, Br^-, Cl^-, (NO_3^-, SO_4^{--}) in the order given.

2) P. Delahay, *J. Am. Chem. Soc.*, **75**, 1190 (1953).
3) H. Imai and H. Sunahara, Symposium on presented at the Polarography, Hiroshima (1955).
4) Strictly speaking, the assumption is not valid, because iR drop affects v. This assumption holds approximately[5].
5) H. Imai, *J. Electrochem. Soc. Japan*, **23**, 530 (1955)

From the above mentioned results it is reasoned that the surface charge density of is the D. M. E. inversely proportional to the value of $\pi_R - \pi_S$. Here, $\pi_R - \pi_S$ was assumed to be the measure of Coulombic attraction of a metal ion to its colloidal hydroxide. Since a metal ion is attracted both to its hydroxide and to the anion which exists in the electrode surface, it is reasoned that the former attractive force is becoming weaker as the surface charge density of the electrode increases.

In this connection, it was suggested by Heyrovský[6,7] that a halogen ion suffers from a polarization by the negative charge of the electrode. Hence, the electric field exerted on the metal ion results from the polarization of an anion as is illustrated in Fig. 5. Thus, the more polarizable is the anion, the larger is the negative charge represented by $G-G'$. The existence of such a space charge requires an extra applied potential for an electron transfer. (This is best realized by comparing the function of $G-G'$ with that of the grid of a triode vacuum tube.). Thus, the shift of the peak potential listed in Tables I, II and III can be explained. In the same manner, it can be expressed

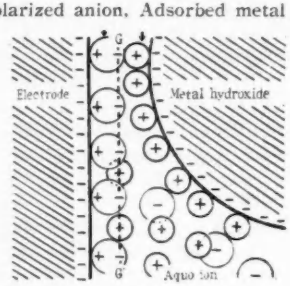


Fig. 5. Schematic representation of the electrode surface.

that the more polarizable is the adsorptive anion layer, the less is the attractive force between the inner metal ion and the colloidal metal hydroxide.

The author wishes to express his hearty gratitude to Prof. Mutsuaki Shinagawa for his valuable advice and encouragement.

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6) J. Heyrovsky, *Discs. Faraday Soc.*, **1**, 212 (1947).
7) J. Heyrovsky, *Wien. Chem. Ztg.*, **48**, 24 (1947).

SHORT COMMUNICATIONS

On the Relative Volatility of Heavy- and Light-oxygen Water

By Sadahiro SAKATA and Noriyoshi MORITA

(Received October 3, 1955)

As concerns the relative volatility of heavy- and light-oxygen water at 100°C, M. H. Wahl and H. C. Urey[1] obtained a value of 1.003 by extrapolating their experimental values measured at four temperatures between 11.25 and 46.35°C, and this value has been accepted. Recently, H. E. Watson[2] analysed the results of his experiments on the concentration of light oxygen water and concluded that a value of 1.0056 is the most probable one for the relative volatility of H_2O^{16} and H_2O^{18}. He quoted for comparison the values between 1.0046 and 1.0062 which were obtained by several other authors. During our experiments on the concentration of heavy oxygen by the fractional distillation of water, we became aware of the fact that the degree of enrichment of the heavy oxygen was excessive as compared with that of the deuterium, so far as the value of 1.003 was used as the single plate fractionation factor for heavy oxygen. Therefore we attempted to verify the relative volatility by the following experiments.

A packed column is operated at total reflux under atmspheric pressure. Distillation is started with 4l of normal water in the pot. As distillation is continued, the same volume of normal water as that of distillate is refluxed at the top of the column. Thus, at intervals small quantities of water sample (about 30 cc. each time) are taken out of the pot and their contents in heavy oxygen and deuterium are measured separately. Assum-

ing that the plate efficiencies are equal for isotopes of oxygen and hydrogen, and that the fractionation factor for H_2O/HDO is 1.0260, we can obtain the apparent fractionation factors each time of sampling for heavy oxygen water by applying Fenske equation. Some of the results obtained are tabulated in the accompanying table.

Duration of operation days	Excess density due to		Number of plates in Fenske eq. based on deuterium	Apparent fractionation factor for heavy oxygen
	deuterium γ	heavy oxygen γ		
24	14.9	36.2	25.9	1.0058
38	24.4	46.2	36.4	1.0052
46	25.9	49.4	37.8	1.0053
55	29.5	54.2	41.0	1.0053
63	32.2	56.1	43.3	1.0052
80	39.5	59.0	48.8	1.0048
88	41.3	59.1	50.0	1.0047
95	43.7	59.5	51.8	1.0045

As will be seen in the table, the apparent fractionation factor for oxygen isotope diminishes gradually as the fractionation proceeds toward equilibrium. This fact may indicate that the concentrations of heavy oxygen and deuterium in water do not proceed at the same rate, but that heavy oxygen reaches equilibrium earlier than deuterium. Time (t) necessary for equilibration can be calculated by the equation advanced by H. C. Urey, et. al.[3]:

$$t=\frac{H\left\{(1-N)\ln\frac{1-N}{1-N_0}+N\ln\frac{N}{N_0}\right\}}{wN(\alpha-1)k\ln\alpha}+\frac{h(N_0-N)}{wN(\alpha-1)}$$

Here, N and N_0 denote the mole fraction of the less-volatile component at the top and the bottom, H and h are the hold-up in the column and the pot, w is the through-put, α is the single plate fractionation factor, and k is the number of theoretical plates. Under our experimental conditions t's are calculated to be about 39 days for heavy oxygen and about 78 days for deuterium, i. e. the former reaches equilibrium twice as rapidly as the latter. The experimental results show a longer time than that mentioned for equilibration but their tendency is in accord with the prediction.

In conclusion, it is quite clear that the value of 1.003 obtained by Wahl and Urey is too low. However, the value of 1.0056 obtained by Watson seems too high because his calculation might be based on an incorrect plate number which was determined by the non-equilibrated concentration of deuterium.

Recently the following relation for the relative volatility and the temperature T in °K is presented[4]:

$$\log(p_{H_2O^{18}}/p_{H_2O^{16}})=3.20/T-0.00680$$

According to this equation, the relative volatility is 1.0041 for 100°C. Extrapolating our experimental results, we can also conclude that the correct value may lie between 1.0043 and 1.0040. In another experiment done under a larger through-put, we obtained a value of 1.0043.

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1) M. H. Wahl and H. C. Urey, *J. Chem. Soc.*, 3, 411 (1935).
2) H. E. Watson, *J. Appl. Chem.*, 3, 556 (1953).
3) H. C. Urey, J. R. Huffman, H. C. Thode, and M. Fox, *J. Chem. Phys.*, 5, 856 (1937).
4) I. Kirschenbaum, "Physical Properties and Analysis of Heavy Water", McGraw-Hill Book Co. Inc., New York, N. Y. (1951), p. 29.

Über die unmittelbare Messung von den Zuständen in die Ionenaustauschharzphase adsorbierter Komplexionen mit den Harzmembranen

Von Masatoshi FUJIMOTO

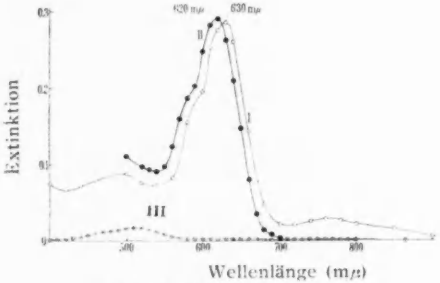
(Eingegangen am 6. Oktober, 1955)

Whnn die gefärbten Komplexionen ins farblosen Ionenaustauschharz adsorbiert werden, färbt sich das Harz häufig ganz verschieden von der Farbe der wässerigen Lösungen. Diese Verschiedenheit der Färbung beruht vermutlich auf den besonderen Zuständen in die Harzphase adsorbierter Komplexionen.

Sehr interessantes Beispiel dafür bietet eine charakteristische himmelblaue Färbung, die die wässerige Lösung der Kobalt(II)rhodanide in Berührung mit einer farblosen starkbasischen Anionenaustauschharz liefert. Diese himmelblaue Färbung ist derjenigen von den Komplexsalzen ganz ähnlich, die mit dem organischen Lösungsmittel, z. B. einem Gemisch des Äthyläthers und Isoamylalkohols, ausgezogen werden, und diese Färbung ist auch zum Nachweis geringer Menge des Kobaltes anwendbar[1].

Um diese charakteristische Färbung direkt und quantitativ zu bestimmen, hat der Verfasser erstens mit einer Suspension[2]

starkbasisches Anionenaustauschharzes, Dowex 1-X4, einfacheV ergleichung von der Extinktion, mit Komplexionen ausgetauschter Harzsuspension und von derjenigen der Harzsuspension von Chloridform durchgeführt. Abb. I. stellt ein Resultat dar, worin eine gewisse Ähnlichkeit zwischen den Zuständen in die Harzphase adsorbierter Kobalt(II)-rhodanidkomplexe und denjenigen mit organischem Lösungsmittel ausgezogener Komplexe deutlich gezeigt wird. Jedoch, durch diese Methode konnte man nicht immer ein konstantes Ergebnis erhalten, weil es sehr schwierig ist, Suspension des Harzes von gleicher und sehr feinster Korngrösse herzustellen.



Wellenlänge (mμ)

Abb. I. Lichtabsorption der Harzsuspension.

I.-Kurve. Harzsuspension: (1 ccm Harzsuspension(A) + Probelösung + Wasser → 10 ccm)-Lösung verglichen mit (1 ccm Harzsuspension(A) + Wasser → 10 ccm)-Lösung.

Harzsuspension(A):—

Man zerreibt 0.2 g Dowex 1-X4 mit geringer Menge destilliertes Wassers völlig, verdünnt das Gemisch mit destilliertem Wasser genau zu 10.0 ccm, schüttelt danach um, und lässt sie 10 Min lang stehen.

Probelösung:—$CoCl_2$ 0.0039 M, NH_4SCN 0.023 M, HCl 0.0020 M, pH 3.81. ($CoCl_2$ = 195 γ).

Spektrophotometer:—Beckman DU Typus Spektrophotometer.

II.-Kurve. Die mit organischem Lösungsmittel extrahierte Lösung:

Lösungsmittel:—Äthyläther 1.00 Vol. + Isoamylalkohol 3.00 Vol. ·····(B)

Probelösung:—$CoCl_2$ (114 γ Co/ccm)-

Lösung 1 ccm + { 20% H_3PO_4 2 ccm; 70% CH_3COONH_4 0.5 ccm; 60% NH_4SCN 2.0 ccm } + H_2O → 10 ccm ·····(C)

Mit (B) extrahiert man (C) und verdünnt es genau zu 10.0 ccm mit (B).

III.-Kurve. Dieselbe Probelösung für I.-Kurve, aber nur verdünnt mit Wasser:

Kürzlich, stellte der Verfasser ein Paar einfacher Küvette mit einer hellgelben und halbdurchsichtigen starkbasischen Anionenaustauschharzmembran[2] zur Lichtabsorptionsmessung auf (Abb. II.), um die Extinktion von den in die Harzphase adsorbierten Komplexionen genauer und ohne obenerwähnte Schwierigkeit zu bestimmen. Die Resultate der Messungen werden in Abb. III. zusammen dargestellt.

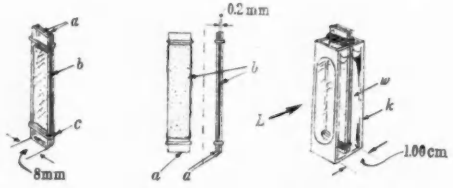
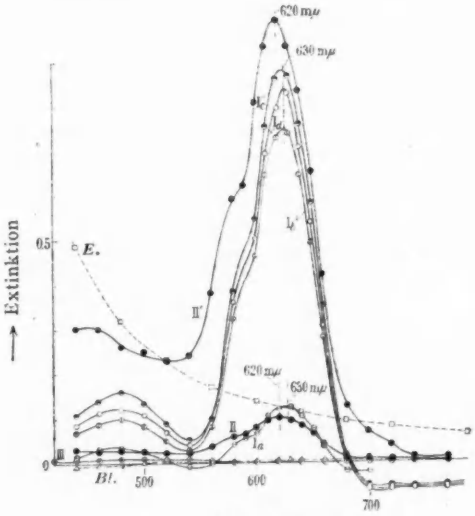


Abb. II. Harzmembranküvette zur Lichtabsorptionsmessung.

a: Mikroskopsobjektglas; *b*: Harzmembran; *c*: Kautschukband; *k*: Küvette für Spektrophotometrie; *w*: destilliertes Wasser; →*L*: Richtung des monochromatischen Lichtes.



Wellenlänge (mμ)

Abb. III. Absorptionsspektra der ins Harzmembran adsorbierten Komplexionen.

I.-Kurve. Absorptionsspektra mit den Kobaltrhodanidkomplexe ausgetauschter Harzmembran verglichen mit Harzmembran von Chloridform:[3]

a: ⊖ 30 Min
b: ◐ 18 Std
c: ● 66 Std
d: ○ 164 Std

nach dem Eintauchen der Harzmembran in die Probelösung.

II.-Kurve. Absorptionsspektra der Probelösung, die in Gegenwart überschüssiges Ammoniumrhodanides mit organi-

schem Lösungsmittel (vgl. (B) über II.-Kurve von Abb. I.) ausgezogen wird:

II'.-Kurve. II.-Kurve zehnfach vergrössert:

III.-Kurve. (⊙) Absorptionskurve der Probelösung:

Bl. Absorption für Probe benutzter Harzmembran (RCl) verglichen mit der für Wasser benutzten Membran (RCl):

E. Absorption für Probe benutzter Harzmembran (RCl) verglichen mit destilliertem Wasser:

Probelösung:—Co^{2+} 0.00025 M, SCN^- 0.1045 M, pH 2.18. (Co^{2+} = 150 γ).

Harzmembran:—10mm×38mm×0.2mm: Mit Kaliumchloridlösung wird sie in die Chloridform übergeführt.

Wie man in Abb. I. und III. leicht sieht, ist es sehr interessant, dass die Gestalt der Lichtabsorptionskurve der in die Harzphase adsorbierten Komplexionen derjenigen ins organische Lösungsmittel ausgezogener Komplexe bedeutend ähnlich ist, und dass die erste Kurve immer „red shift" von etwa 10 mμ gegen die zweite hat[4].

Diese unmittelbare Messung der Lichtabsorption von der Ionenaustauschharzphase mit Hilfe farbloser Harzmembrane[2] wird eine neue und sehr geeignete Methode zur Bestimmung von den Zuständen ins Ionenaustauschharz adsorbierter verschiedenartiger Komplexionen bieten.

Für die Harzmembran ist der Verfasser Herrn Prof. Dr. T. Kuwada zu grossem Dank verpflichtet.

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1) M. Fujimoto, Dieses Bulletin, 27, 48 (1954).

2) Durch völliges Zerreiben der mit geringer Menge destilliertes Wassers angefeuchteten Harzkörnchen kann man diese Harzsuspension verhältnismässig leicht herstellen.

3) Eine aus künstlicher Kautschukmembran dargestellte starkbasische Anionenaustauschharzmembran von quartärem Ammoniumtypus: (Nach der Privatmitteilung von Herrn S. Yoshikawa). Als der Kontrast von der Absorptionsmessung wird die obengenannte Harzmembran angewendet, die nur mit Kaliumchloridlösung in die Chloridform übergeführt wird. Zur Zeit führt der Verfasser noch eingehende Untersuchung über die Einflüsse verschiedener Bedingungen, darauf die Veränderung der Quellung und der Durchsichtigkeit von Harzmembran beruht, sowie die der Neigung der Membranfläche gegen die Richtung des Lichtes durch.

4) Man könnte vermuten, dass diese Wellenlängendifferenz der Absorptionsbäuder hauptsächlich auf irgendeiner Wirkung zwischen den Rhodanidionen und den Harzkationen beruht, worüber doch man später eingehende Untersuchungen durchführen müsse.

Copolymerization of Optically Active Ethyl 2-Methyl-2-ethyl-2-butenoate with Vinyl Acetate

By Matsuji TAKEBAYASHI and Yasumasa ITO

(Received November 19, 1955)

In order to investigate the steric effect on the radical polymerization of vinyl compounds, we have prepared ethyl 2-methyl-2-ethyl-2-butenoate (Et-MEB)* which has an optical center nearest to the vinyl group, and studied the polymerization of the ester at 60°C. in the presence of benzoyl peroxide. The ester polymerized only slightly by itself, while it polymerized to a certain extent with vinyl acetate (VAc) under the experimental conditions. A sample of (+)-Et-MEB, the optical purity of which was 75%, was resolved by using brucine from (±)-Et-MEB, and the monomer reactivity ratios, r_1 and r_2, in the copolymerization of (+)-Et-MEB with VAc were compared with those in the same reaction of (±)-Et-MEB with VAc. The results obtained are given in the following table.

Monomer Reactivity Ratio within the Limits of [VAc]/[Et-MEB]=1–3

In the case of	Monomer reactivity ratio
(±)-Et-MEB and VAc	$r_1=k_1/k_2=3.2\pm0.5$, $r_2=k_3/k_4=0.3\pm0.2$
(+)-Et-MEB and VAc	$r_1=k_1/k_2=2.2\pm0.4$, $r_2=k_3/k_4=0.1\pm0.1$

where k_1, k_2, k_3 and k_4 indicate the rate constant of the reactions (1), (2), (3) and (4), respectively.

$$\cdots\cdots VAc\cdot + VAc \xrightarrow{k_1} \cdots\cdots VAc\cdot \quad (1)$$

$$\cdots\cdots VAc\cdot + Et\text{-}MEB \xrightarrow{k_2} \cdots\cdots Et\text{-}MEB\cdot \quad (2)$$

$$\cdots\cdots Et\text{-}MEB\cdot + Et\text{-}MEB \xrightarrow{k_3} \cdots\cdots Et\text{-}MEB\cdot \quad (3)$$

$$\cdots\cdots Et\text{-}MEB\cdot + VAc \xrightarrow{k_4} \cdots\cdots VAc\cdot \quad (4)$$

The data in the table suggest that the reactivity of (+)-Et-MEB on the radical of VAc-type may be about 1.5 times as large as that of (±)-Et-MEB in the reaction (2), because no steric effect will appear on the rate of reactions (1) and (4).

Assuming that the acetyl group of polyvinyl acetate is arranged over five to six units of vinyl acetate at least in such an orientation as has been recognized in that of hydroxyl group of polyvinyl alcohol, a similar orientation will also be given to the acetyl group of the growing copolymeric radicals.

Then it may be possible that the reactivity of (+)-Et-MEB on the growing radical of VAc-type is different from that of (±)-Et-MEB.

The details of this study will be reported in a separate paper.

We express our hearty thanks to Prof. S. Murahashi and Prof. S. Okamura for their kind advice and to the Ministry of Education for a Grant-in-Aid for Scientific Research.

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* The physical properties of the ester were found as follows: b.p.$_{50}$ 82.0°C., d_4^{20} 0.89423, n_D^{20} 1.4290.